

# The Realizations of Some Purely Discontinuous Stochastic Processes

by  
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**1. Summary.** We consider a real stochastic process  $\{x_t, t \in I_0\}$ , where  $I_0$  is a closed finite interval.  $x_t$  are functions of two arguments and can be explicitly written in the form  $x_t(\omega)$ , where  $t \in I_0$  and  $\omega \in \Omega$ ,  $\Omega$  being the set of elementary events. We assume that the process considered is separable ([3] p. 51) and, further, that the process  $\{x_t, t \in I_0\}$  has no fixed discontinuity points, i. e. that

$$(1) \quad P[\lim_{s \rightarrow t} x_s(\omega) = x_t(\omega)] = 1 \quad (t \in I_0).$$

The main result of this paper is to establish that if relation (5) given below is satisfied, the  $\omega$  set for which the  $x_t(\omega)$  are step functions has probability 1. In other words, almost every realization  $x_t(\omega)$  has only a finite number of points of discontinuity, and is constant in every open interval of continuity points; in addition, at each discontinuity point exist both left- and right-hand limits. It is, moreover, shown that the mathematical expectation of the number of discontinuities is then finite and an explicit expression for this is given (Theorem 1).

**2.** We shall introduce the following notations. By  $x_I$  we shall denote the increment of  $x_t$  over the interval  $I$  and by  $|I|$  the length of the interval  $I$ , where  $I \subset I_0$ . By  $\xi(I)$  we shall denote the number of discontinuities of  $x_t$  in  $I$ , where  $\xi(I) = \infty$ , if the number of discontinuities is not finite. Further, we shall denote

$$(2) \quad a(I) = P(x_I \neq 0),$$

$$(3) \quad A(I) = \lim_{n \rightarrow \infty} \sum_{k=1}^n a(I_{nk}),$$

when  $\max_{1 \leq k \leq n} |I_{nk}| \rightarrow 0$ , where  $\{I_{nk}\}$  is a partition of  $I$  into non-overlapping intervals  $I_{nk}$ .  $A(I)$  is the Burkil integral of  $a(I)$ . The upper Burkil inte-

gral  $\bar{A}(I)$  of  $a(I)$  is obtained by replacing in (3) the symbol  $\lim$  by  $\overline{\lim}$ . The derivative of  $a(I)$  at the point  $t \in I$  will be denoted by  $Q(t)$ , i. e.

$$(4) \quad Q(t) = \lim_{|I| \rightarrow 0} \frac{a(I)}{|I|},$$

as  $I$  contracts to a fixed point  $t \in I$ .

We shall introduce the following

**Definition.** The process  $\{x_t, t \in I_0\}$  is *purely discontinuous* if the  $\omega$  set  $A$  for which the  $x_t(\omega)$  have the property:

for each  $t \in I_0$  there exists a  $\delta(t, \omega) > 0$  such that for each  $t'$  satisfying the inequality  $|t - t'| < \delta(t, \omega)$  the equality  $x_{t'}(\omega) = x_t(\omega)$  holds, unless  $x_t(\omega)$  has a discontinuity at  $t$ ,

satisfies the equality  $P(A) = 1$ .

The following theorems hold.

**THEOREM 1.** Let the stochastic process  $\{x_t, t \in I_0\}$  be separable and without fixed discontinuity points. If the relation

$$(5) \quad \bar{A}(I) < \infty$$

holds, then for every open interval  $I \subset I_0$ :

(i) the process is purely discontinuous;

(ii) the mathematical expectation  $E\xi(I)$  exists, is finite and satisfies the relations

$$(6) \quad E\xi(I) = \bar{A}(I) = A(I) < \infty;$$

(iii) the  $\omega$  set such that at the discontinuities of  $x_t(\omega)$  (if any) both left- and right-hand limits exist, has probability 1;

(iv) the derivative  $Q(t)$  exists almost everywhere and the relation

$$(7) \quad \int_I Q(t) dt \leq A(I)$$

holds.

**THEOREM 2.** Let the process  $\{x_t, t \in I_0\}$  be separable, without fixed discontinuity points, and let  $a(I)$  be an absolutely continuous function\*) of an interval. Then the assertions of Theorem 1 hold, and moreover the relation

$$(8) \quad \int_I Q(t) dt = A(I)$$

is satisfied.

From Theorem 2 follows the

**COROLLARY.** If the process  $\{x_t, t \in I_0\}$  is separable, without fixed discontinuity points and if  $a(I)$  satisfies the Lipschitz condition, i. e., if there exists

\*) The function  $a(I)$  of an interval is absolutely continuous if to each  $\varepsilon > 0$  there corresponds such a  $\delta > 0$  that the relation  $\sum |I_k| < \delta$  implies the relation  $\sum a(I_k) < \varepsilon$ , where  $\{I_k\}$  is a partition of  $I$  in non-overlapping intervals.



such a constant  $K > 0$  that for all  $I \subset I_0$  the inequality

$$(9) \quad a(I) < K|I|$$

holds, then the assertions of Theorem 2 hold.

A condition for the existence of a finite  $E\xi(I)$  for Markov processes with a finite number of states, similar to (5) but not the same, has been given by Dobrushin ([2] p. 543).

The converse of Theorem 1 is not true. One can give examples of separable stochastic processes without fixed discontinuity points for which  $E\xi(I) < \infty$ , and relation (5) does not hold nevertheless. The following theorem, which is in some sense a converse of Theorem 1, holds.

**THEOREM 3.** *Let the stochastic process  $\{x_t, t \in I_0\}$  be separable, without fixed discontinuity points and let it be purely discontinuous. If  $E\xi(I)$  exists and is finite, relation (5) holds and consequently relation (6) also holds.*

The proofs of these theorems will appear in *Studia Mathematica*. In these proofs, properties of Burkil integrals found by Burkil [1] and Saks [4] are used.

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#### REFERENCES

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- [2] R. L. Dobrushin, *Regularity conditions for Markov processes with a finite number of possible states* Mat. Sbornik **34** (1954), 541.
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# Sur un nouveau type de problèmes pour un système d'équations différentielles hyperboliques du second ordre à deux variables indépendantes

par

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Présenté par T. WAŻEWSKI le 28 Novembre 1955

1. Considérons le système de  $n$  équations différentielles

$$(1) \quad u_{xy}^{(i)}(x, y) = f^{(i)}(x, y, u^{(1)}, \dots, u^{(n)}, u_x^{(1)}, \dots, u_x^{(n)}, u_y^{(1)}, \dots, u_y^{(n)}) \quad (i=1, \dots, n),$$

que nous écrirons dans la suite sous la forme vectorielle

$$(2) \quad U_{xy}(x, y) = F(x, y, U, U_x, U_y).$$

Supposons que  $F(x, y, U, P, Q)$  soit une fonction vectorielle continue dans l'ensemble  $\Pi$  défini par les inégalités \*)

$$0 \leq x \leq a \quad \text{et} \quad 0 \leq y \leq \beta, \quad \text{où} \quad 0 < a < \infty \quad \text{et} \quad 0 < \beta < \infty,$$

$$|U| \leq r, \quad |P| \leq r \quad \text{et} \quad |Q| \leq r, \quad \text{où} \quad 0 < r < \infty.$$

Considérons deux courbes continues  $\Gamma$  et  $\Lambda$

$$y = \gamma(x) \quad 0 \leq x \leq a,$$

$$x = \lambda(y) \quad 0 \leq y \leq \beta,$$

situées dans le rectangle  $D$

$$0 \leq x \leq a, \quad 0 \leq y \leq \beta.$$

Envisageons les problèmes concernant l'existence d'une solution  $U(x, y)$  du système (2) ayant les dérivées  $U_x, U_y, U_{xy}$  continues dans

\*) La norme du vecteur  $V = (v^{(1)}, \dots, v^{(n)})$  est donnée par la formule  $|V| = \sup_{1 \leq i \leq n} |v^{(i)}|$ .



le rectangle  $D$  et satisfaisant le long des deux courbes  $\Gamma$  et  $A$  à certaines relations données. Chacun de tels problèmes sera dit du type  $T^*$ ).

2. Voici maintenant deux problèmes suivants du type  $T$ :

Problème I. Existe-t-il une solution  $U(x, y)$  du système (2) ayant les dérivées  $U_x, U_y, U_{xy}$  continues dans  $D$  et satisfaisant aux conditions

$$U(x_0, y_0) = \overset{0}{U},$$

$$U_x(x, \gamma(x)) = G[x, U(x, \gamma(x)), U_y(x, \gamma(x))] \quad \text{lorsque} \quad 0 \leq x \leq a,$$

$$U_y(\lambda(y), y) = H[y, U(\lambda(y), y), U_x(\lambda(y), y)] \quad \text{lorsque} \quad 0 \leq y \leq \beta,$$

où  $(x_0, y_0)$  est un point arbitraire de  $D$ ,  $\overset{0}{U}$  est un vecteur constant et  $G(x, U, Q)$ ,  $H(y, U, P)$  sont des fonctions continues données d'avance?

Problème II. Existe-t-il une solution  $U(x, y)$  du système (2) ayant les dérivées  $U_x, U_y, U_{xy}$  continues dans  $D$  et satisfaisant aux conditions

$$U_x(x, \gamma(x)) = G[x, U(x, \gamma(x)), U_y(x, \gamma(x))] \quad \text{lorsque} \quad 0 \leq x \leq a,$$

$$U(\lambda(y), y) = B(y) \quad \text{lorsque} \quad 0 \leq y \leq \beta,$$

où  $G(x, U, Q)$  et  $B(y)$  sont des fonctions continues données d'avance?

On vérifie facilement que l'existence d'une solution du problème I résulte de celle d'une solution de classe  $C^1$  du système

$$(3) \quad U(x, y) = L[U] \equiv \overset{0}{U} + \int_{x_0}^x G[s, U(s, \gamma(s)), U_y(s, \gamma(s))] ds + \\ + \int_{y_0}^y H[t, U(\lambda(t), t), U_x(\lambda(t), t)] dt + \\ + \int_{x_0}^x \left\{ \int_{\gamma(s)}^{y_0} F[s, t, U(s, t), U_x(s, t), U_y(s, t)] dt \right\} ds + \\ + \int_{y_0}^y \left\{ \int_{\lambda(t)}^x F[s, t, U(s, t), U_x(s, t), U_y(s, t)] ds \right\} dt$$

et que l'existence d'une solution du problème II résulte de celle d'une solution de classe  $C^1$  du système

\*) À la séance du 30 Septembre 1955 de la Conférence consacrée aux équations différentielles aux dérivées partielles (Cracovie, 26 Sept. — 1 Oct. 1955), j'ai présenté la méthode de résoudre certains problèmes formulés dans la communication présente. J'ai caractérisé en détail le mécanisme de cette méthode aux séances du 13 Octobre et 20 Octobre 1955 du Groupe des Equations Différentielles de l'Institut Mathématique de l'Académie Polonaise des Sciences (Section de Cracovie).

Les démonstrations détaillées et autres théorèmes concernant les problèmes du type  $T$  seront publiés ailleurs.

$$(4) \quad U(x, y) = \mathcal{L}[U] \equiv B(y) + \int_{\lambda(y)}^x G[s, U(s, \gamma(s)), U_y(s, \gamma(s))] ds + \\ + \int_{\lambda(y)}^x \left\{ \int_{\gamma(s)}^y F[s, t, U(s, t), U_x(s, t), U_y(s, t)] dt \right\} ds.$$

J'ai démontré, sous certaines hypothèses, l'existence d'une solution de classe  $C^1$  de chacun des systèmes (3) et (4) en appliquant le théorème de Schauder \*) aux transformations  $\tilde{U} = L[U]$  et  $\tilde{U} = \mathcal{L}[U]$  respectivement et aux ensembles  $Z$  et  $\mathcal{Z}$  convenablement choisis dans l'espace  $C^1$ .

Vue la brièveté de cette communication, je n'énonce en toute précision que deux théorèmes concernant des cas particuliers des problèmes I (Théorème 1) et II (Théorème 2).

Hypothèse K. La fonction  $F(x, y, U, P, Q)$ , continue dans l'ensemble  $\Pi$ , y satisfait à la condition \*\*)

$$(5) \quad |F(x, y, U, \bar{P}, \bar{Q}) - F(x, y, U, P, Q)| \leq \omega(y, |P - \bar{P}|, x) + \omega(x, |Q - \bar{Q}|, y),$$

où  $\omega(z, v, \tau)$  est une fonction continue assujettie dans l'ensemble  $0 \leq z \leq h$ ,  $v \geq 0$ ,  $0 \leq \tau \leq h$ , où  $h = \max(a, \beta)$ , aux conditions suivantes:

1°  $\omega(z, v, \tau)$  est non décroissante par rapport à  $v$ ;

2°  $\omega(z, 0, \tau) = 0$  pour  $0 \leq z \leq h$  et  $0 \leq \tau \leq h$ ;

3° pour chaque  $\tau$  fixé dans l'intervalle  $[0, h]$ , par chaque point  $(\tilde{z}, \tilde{v})$ ,  $0 \leq \tilde{z} \leq h$ ,  $\tilde{v} \geq 0$  passe une intégrale unique de chacune de deux équations

$$dv/dz = \omega(z, v, \tau) \quad \text{et} \quad dv/dz = -\omega(z, v, \tau).$$

THÉORÈME 1. Admettons l'hypothèse K. Supposons que \*\*\*)

$$(6) \quad N = \max_{(m)} |F| \leq \min \{r/h, r/2h^2\} \quad \text{où} \quad h = \max(a, \beta),$$

et choisissons un nombre  $a \geq 0$  tel que

$$(7) \quad a \leq \min \{r - hN, (r - 2Nh^2)/(1 + 2h)\}.$$

\*) [1] Satz 1, p. 173.

\*\*) À la séance du Groupe d'Analyse de l'Institut Mathématique de l'Académie Polonaise des Sciences (Varsovie 1954), S. Mazur a démontré, en se servant du théorème de Schauder mentionné ci-dessus, l'existence d'une solution du problème de Darboux relatif à l'équation  $u_{xy}(x, y) = f(x, y, u, u_x, u_y)$  sous l'hypothèse que la fonction  $f(x, y, u, p, q)$  vérifie la condition de Lipschitz par rapport à  $p$  et  $q$ . La condition (5) est moins restrictive que celle de Lipschitz relative à  $P$  et  $Q$ ). Je dois à A. Plis l'idée d'introduire cette hypothèse de régularité.

\*\*\*) Lorsque la fonction  $F$  est bornée dans l'ensemble  $(x, y) \in D$  et  $U, P, Q$  arbitraires, l'inégalité (6) subsiste pour les  $r$  suffisamment grands. Il en résulte que le nombre  $a$  satisfaisant (7) peut être choisi arbitrairement.



Soit  $A(x_0, y_0)$  un point arbitraire du rectangle  $D$ . Supposons que le vecteur constant  $\overset{0}{U}$  et les fonctions vectorielles continues  $G^*(x)$  et  $H^*(y)$  satisfont aux inégalités  $|\overset{0}{U}| \leq a$  et

$$|G^*(x)| \leq a \quad \text{lorsque} \quad 0 \leq x \leq a, \quad |H^*(y)| \leq a \quad \text{lorsque} \quad 0 \leq y \leq \beta.$$

Dans ces hypothèses, il existe une solution  $U(x, y)$  du système (2) ayant les dérivées  $U_x, U_y, U_{xy}$  continues dans  $D$  et satisfaisant aux conditions

$$U(x_0, y_0) = \overset{0}{U} \quad \text{et} \quad U_x(x, \gamma(x)) = G^*(x) \quad \text{lorsque} \quad 0 \leq x \leq a, \\ U_y(\lambda(y), y) = H^*(y) \quad \text{lorsque} \quad 0 \leq y \leq \beta.$$

THÉORÈME 2. Admettons l'hypothèse  $K$ . Soit  $s$  un nombre quelconque non négatif. Supposons que

$$N = \max_{(II)} |F| \leq \min \{r/h, r/h^2, r/h(1+s)\} \quad \text{où} \quad h = \max(a, \beta)$$

et choisissons un nombre  $a \geq 0$  tel que

$$a \leq \min \{r - hN, (r - Nh^2)/(1+h), (r - Nh - Nhs)/(1+s)\}.$$

Supposons que la courbe  $A$  soit de classe  $C^1$ , que

$$-s \leq \lambda'(y) \leq s \quad \text{lorsque} \quad 0 \leq y \leq \beta,$$

et que les fonctions vectorielles continues  $G^*(x), B(y), B'(y)$  satisfont aux inégalités

$$|G^*(x)| \leq a \quad \text{lorsque} \quad 0 \leq x \leq a, \\ |B(y)| \leq a \quad \text{et} \quad |B'(y)| \leq a \quad \text{lorsque} \quad 0 \leq y \leq \beta.$$

Dans ces hypothèses, il existe au moins une solution  $U(x, y)$  du système (2) ayant les dérivées  $U_x, U_y, U_{xy}$  continues dans  $D$  et satisfaisant aux conditions

$$U_x(x, \gamma(x)) = G^*(x) \quad \text{lorsque} \quad 0 \leq x \leq a, \\ U(\lambda(y), y) = B(y) \quad \text{lorsque} \quad 0 \leq y \leq \beta.$$

Nous ne nous occuperons dans la suite que de la démonstration du Théorème 1, car celles des théorèmes concernant les autres problèmes du type  $T$  sont au fond analogues.

Soit  $\delta(\varepsilon)$  le module de continuité\*) commun de la fonction  $F(x, y, U, P, Q)$  dans l'ensemble  $II$ , des fonctions  $G^*(x), \gamma(x)$  dans l'inter-

\*)  $R(\Xi)$  étant fonction arbitraire (vectorielle ou non), définie dans un ensemble  $\Omega$ , une fonction non décroissante  $\delta(\varepsilon)$  est dite *module de continuité* de la fonction  $R(\Xi)$  lorsque  $\delta(\varepsilon) \rightarrow 0$  pour  $\varepsilon \rightarrow 0$  et que  $\delta(\varepsilon) \geq \sup |R(\Xi) - R(\hat{\Xi})|$  pour tous  $\Xi, \hat{\Xi} \in \Omega$  tels que  $|\Xi - \hat{\Xi}| \leq \varepsilon$ .



valle  $[0, a]$  et des fonctions  $H^*(y)$ ,  $\lambda(y)$  dans l'intervalle  $[0, \beta]$ . Posons

$$\mu(\varepsilon) = (1 + N)\delta(\varepsilon) + h[\delta(\varepsilon) + \delta(r\varepsilon) + \delta(N\varepsilon)].$$

Désignons par  $v = \chi_1(y, \xi, \eta; x)$  l'intégrale de l'équation  $dv/dy = \omega(y, v, x)$  ( $x$  étant fixé dans l'intervalle  $[0, a]$ ) issue du point  $(\xi, \eta)$  et par  $v = \chi_2(y, \xi, \eta; x)$  celle de l'équation  $dv/dy = -\omega(y, v, x)$  passant par le même point. Soit

$$\psi(y, x, \varepsilon) = \begin{cases} \chi_1(y, \gamma(x), \mu(\varepsilon); x) & \text{lorsque } y \geq \gamma(x) \\ \chi_2(y, \gamma(x), \mu(\varepsilon); x) & \text{lorsque } y < \gamma(x). \end{cases}$$

D'une manière analogue, définissons une fonction  $\varphi(x, y, \varepsilon)$  en échangeant dans la définition précédente le rôle de  $x$  et de  $y$  et en y remplaçant  $\gamma(x)$  par  $\lambda(y)$  de même que  $a$  par  $\beta$ .

Considérons dans l'espace  $C^1$  l'ensemble  $Z^*$  des fonctions  $U(x, y)$  définies dans le rectangle  $D$  et y satisfaisant aux inégalités

$$|U(x, y)| \leq r, \quad |U_x(x, y)| \leq r, \quad |U_y(x, y)| \leq r,$$

$$|U_x(x, \bar{y}) - U_x(x, \bar{\bar{y}})| \leq N|\bar{y} - \bar{\bar{y}}|, \quad |U_y(\bar{x}, y) - U_y(\bar{\bar{x}}, y)| \leq N|\bar{x} - \bar{\bar{x}}|,$$

$$|U_x(\bar{x}, y) - U_x(\bar{\bar{x}}, y)| \leq \psi(y, \bar{x}, |\bar{x} - \bar{\bar{x}}|),$$

$$|U_y(x, \bar{y}) - U_y(x, \bar{\bar{y}})| \leq \varphi(x, \bar{y}, |\bar{y} - \bar{\bar{y}}|).$$

En s'appuyant sur le théorème de Schauder (cf. le renvoi \*) p. 69), on démontre l'existence dans l'ensemble  $Z^*$  d'un point fixe de la transformation  $\tilde{U}(x, y) = L^*[U]$ , où  $L^*[U]$  est une opération obtenue de  $L[U]$  (définie dans (3)), lorsqu'on y remplace  $G(x, U, Q)$  par  $G^*(x)$ , et  $H(y, U, P)$  par  $H^*(y)$ . Le Théorème 1 se trouve ainsi démontré.

3. Remarque 1. Le problème de Darboux équivaut à ceux qui sont des cas particuliers des problèmes du type  $T$  considérés dans les théorèmes 1 ( $\gamma(x) \equiv 0$ ,  $\lambda(y) \equiv 0$ ,  $(x_0, y_0) \equiv (0, 0)$ ) et 2 ( $\gamma(x) \equiv 0$ ,  $\lambda(y) \equiv 0$ ). Il en est de même du problème de Cauchy ( $\gamma'(x)$  continue,  $\gamma'(x) \neq 0$ ,  $\lambda(y)$  inverse à  $\gamma(x)$ ,  $y_0 = \gamma(x_0)$ ). Le problème de Picard est un cas particulier de celui considéré dans le théorème 2 ( $\gamma(x) \equiv 0$ ,  $\lambda(0) \equiv 0$ ).

Remarque 2. Dans les hypothèses convenables plus restrictives, les problèmes I et II possèdent une solution unique, qui peut être obtenue par la méthode des approximations successives appliquée aux transformations  $\tilde{U} = L[U]$  et  $\tilde{U} = \mathcal{L}[U]$  respectivement (cf. (3) et (4)).

Remarque 3. Les résultats analogues subsistent pour les autres équations différentielles hyperboliques, par exemple pour l'équation presque linéaire.

Remarque 4. Considérons le problème du type  $T$  dans lequel les valeurs de  $U$  sont données le long de deux courbes  $\Gamma$  et  $\Lambda$ . Or, même l'hypothèse de l'analyticité relative aux fonctions  $F, \gamma, \lambda$  et aux valeurs

données n'assure pas l'existence (même locale) de la solution du problème en question (exemple:  $F \equiv 0$ ,  $U(x, x) \equiv 0$ , lorsque  $-h \leq x \leq h$ ,  $U(-y, y) = y^2$  lorsque  $-h \leq y \leq h$ ). Toutefois, j'ai réussi d'établir l'existence de la solution de ce problème dans des hypothèses de régularité assez faibles, mais en admettant l'hypothèse supplémentaire que  $|\lambda'(\gamma(x))\gamma'(x)| < 1$ .

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#### OUVRAGES CITÉS

[1] J. Schauder, *Der Fixpunktsatz in Funktionalräumen*, *Studia Mathematica* 2 (1930), 171.



# Abelian Groups that are Direct Summands of Every Abelian Group which Contains Them as a Pure Subgroup

by

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*Presented by K. KURATOWSKI on December 1, 1955*

Consider class **D** of Abelian groups  $G$  with the following property:  
If  $G$  is a pure subgroup of an Abelian group  $H$ , then  $G$  is a direct summand of  $H$ .

**THEOREM 1.**  $G$  is in **D** if, and only if, there exists an Abelian group  $G'$  such that  $G+G'$  admits a compact (= bicomact) topology.

**THEOREM 2.**  $G$  is in **D** if, and only if,  $G$  is isomorphic to a direct summand of a complete direct sum of groups  $C_{p^\alpha}$  ( $p$  is a prime;  $\alpha=1, 2, \dots$  or  $\infty$ ; the sum may be of arbitrary power of summands).

The following property of the group  $G$  we shall call the *property of finite intersections for linear equations*:

for every system  $U$  of linear equations with free coefficients in  $G$ , if every finite subsystem of  $U$  is solvable in  $G$ , then the whole system  $U$  is solvable in  $G$ .

By means of the theorems of S. Gaacsàlyi [1] it may be shown that

**THEOREM 3.**  $G$  is in **D** if, and only if,  $G$  has the finite intersection property for linear equations.

S. Balcerzyk has shown \*) that class **D** is equal to the class of Kaplansky's algebraically compact groups (see [2], p. 54–56).

Proofs of these theorems will be given in a paper under the same title in *Fundamenta Mathematicae*.

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\*) To appear in *Fundamenta Mathematicae*.





## A Theorem on Mappings of the Sphere into the Projective Space

by

J. W. JAWOROWSKI and K. MOSZYŃSKI

*Presented by K. BORSUK on December 2, 1955*

1. Let  $S_n$  be the  $n$ -dimensional unit sphere in the  $(n+1)$ -dimensional Euclidean space  $E_{n+1}$ , i. e., the set of points  $x \in E_{n+1}$  with  $|x|=1$ . We denote by  $\alpha$  the antipodal mapping of  $S_n$ , i. e.  $\alpha(x)=-x$ . The mapping is a continuous involution of  $S_n$ . The point  $\alpha(x)$  is called the antipode of  $x$ .

Let  $P_n$  be the  $n$ -dimensional projective space, i. e., the set of all unordered pairs  $\{x, -x\}$  with  $x \in S_n$ , and let  $p$  be the mapping of  $S_n$  onto  $P_n$  defined by  $p(x)=\{x, -x\}$ .

The degree of a continuous mapping  $\varphi$  of  $S_n$  into itself or into another  $n$ -dimensional manifold  $M_n$  is denoted by  $d(\varphi)$ . If  $M_n=P_n$  then  $d(\varphi)$  is even, if  $n$  is odd, and  $d(\varphi)=0$ , if  $n$  is even.

**THEOREM 1.** *Let  $n > 1$  and let  $f$  be a continuous mapping of  $S_n$  into  $P_n$ . Then there exists a point  $x_0 \in S_n$ , such that  $f(x_0)=fa(x_0)$ .*

The assumption  $n > 1$  is essential, since  $S_1$  is homeomorphic to  $P_1$ . This theorem is a modification of Borsuk's theorem on antipodes (see [2], p. 178, Satz I); it is suggested by B. Knaster.

The proof will be based on the following theorem

(\*) *Let  $M$  be a compact and locally arcwise connected space, such that every 1-dimensional cycle (with integers as coefficients) lying in  $M$  is homologous to zero in  $M$ . Let  $f$  be a continuous mapping of  $M$  into  $P_n$ . Then there exists a continuous mapping  $\varphi$  of  $M$  into  $S_n$  such that  $f(x)=p\varphi(x)$ , for every  $x \in M$ .*

This theorem seems to be known. It can be deduced, for simply connected  $M$ , from a theorem of fibre bundles theory (see [3], Corollary). However, it can be easily proved immediately, under a more general assumption, which is given above.

The sphere  $S_n$  satisfies the hypotheses of Theorem (\*), if  $n > 1$ .

**2. AUXILIARY THEOREM.** *Let  $\varphi$  be a continuous mapping of  $S_n$  into itself such that, for every  $x \in S_n$ , the points  $\varphi(x)$  and  $\varphi(ax)$  are not antipodal. Then  $d(\varphi)$  is even. Moreover, if  $n$  is even, then  $d(\varphi)=0$ .*

*Proof.* Let us put

$$\psi(x) = \frac{\varphi(x) + \varphi(-x)}{|\varphi(x) + \varphi(-x)|} \quad *)$$

Since  $\varphi(x) \neq -\varphi(-x)$ , for every  $x \in S_n$ ,  $\psi$  is a continuous mapping of  $S_n$  into itself and satisfies the condition

$$\psi(x) = \psi(-x), \quad \text{for every } x \in S_n;$$

and hence  $\psi$  may be considered as a superposition of the mapping  $p$  of  $S_n$  onto  $P_n$  and of the mapping  $g$  of  $P_n$  into  $S_n$ , defined for  $y = \{x, -x\} \in P_n$  by  $g(y) = \psi(x)$ . Therefore  $d(\psi)$  is even and  $d(\psi)=0$ , if  $n$  is even.

Let us observe that

(1) the points  $\varphi(x)$  and  $\psi(x)$  are not antipodal, for every  $x \in S_n$ .

Indeed, if we suppose that, for some  $x \in S_n$ ,  $\psi(x) = -\varphi(x)$ , then

$$\varphi(x) \cdot (1 + |\varphi(x) + \varphi(-x)|) = -\varphi(-x).$$

Since  $|\varphi(x)| = |-\varphi(-x)| = 1$ , it follows that  $|\varphi(x) + \varphi(-x)| = 0$ , which contradicts the assumption  $\varphi(x) \neq -\varphi(-x)$ .

From (1) we conclude that  $\varphi$  and  $\psi$  are homotopic (see [2], p. 179, 1). Hence  $d(\varphi) = d(\psi)$ , and the Auxiliary Theorem is proved.

**COROLLARY 1.** *Let  $\varphi$  be a continuous mapping of  $S_n$  into itself. Then, either there exists a point  $x_0 \in S_n$  such that  $\varphi(x_0) = \varphi a(x_0)$  or there exists a point  $x_0 \in S_n$  such that  $\varphi(x_0) = a\varphi a(x_0)$ .*

*Proof.* Let us suppose that  $\varphi(x) \neq \varphi(-x)$ , for every  $x \in S_n$ . Then by putting

$$\psi(x) = \frac{\varphi(x) - \varphi(-x)}{|\varphi(x) - \varphi(-x)|}$$

we obtain a continuous mapping of  $S_n$  into itself, satisfying the condition  $\psi(-x) = -\psi(x)$ . Hence  $d(\psi)$  is odd (see [2], p. 184). As in the proof of the Auxiliary Theorem, one can show that  $\varphi$  and  $\psi$  are homotopic, and therefore  $d(\varphi)$  is odd.

If  $\varphi(x) \neq -\varphi(-x)$  for every  $x \in S_n$ , then, by the Auxiliary Theorem,  $d(\varphi)$  is even.

**COROLLARY 2.** *Let  $n$  be even. Then, for every essential mapping of  $S_n$  into itself there exists a point  $x_0 \in S_n$  such that  $\varphi a(x) = a\varphi(x)$ , since the degree of an essential mapping of  $S_n$  into itself is different from zero.*

**3. Proof of Theorem 1.** Theorem (\*) provides a continuous mapping  $\varphi$  of  $S_n$  into itself such that  $f = p\varphi$ , i. e.,

$$f(x) = \{\varphi(x), -\varphi(x)\} \quad \text{for every } x \in S_n.$$

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\*) In the sense of operations with points in  $E_{n+1}$ .



By Corollary 1, either for some  $x_0 \in S_n$  it is  $\varphi(x_0) = \varphi\alpha(x_0)$ , or for some  $x_0 \in S_n$  it is  $\varphi(x_0) = -\varphi\alpha(x_0)$ . In both cases  $f(x_0) = p\varphi(x_0) = f\alpha(x_0)$ .

4. From Theorem (\*) one can also deduce the following theorem, which is a slight extension of the well known theorem of Poincaré and Brouwer (see, for instance, [1], p. 481):

THEOREM 2. \*) *Let  $n$  be even. Then there exists no continuous function which assigns to every  $x \in S_n$  a straight line in  $E_{n+1}$  passing through  $x$  and tangent to  $S_n$ .*

Proof. Let us suppose that there exists a continuous function  $g$  defined for  $x \in S_n$  and such that  $g(x)$  is a straight line tangent to  $S_n$  in  $x$ . Let  $f(x) = \{y, -y\}$  be the pair of antipodal points of  $S_n$  in which the straight line passing through the centre  $c$  of  $S_n$  and parallel to  $g(x)$  intersects  $S_n$ . Hence  $f$  is a continuous mapping of  $S_n$  into  $P_n$ . Theorem (\*) provides a continuous mapping of  $S_n$  into itself such that  $f = p\varphi$ , i. e.,  $\varphi(x)$  is one of the points  $y, -y$ . Let  $v(x)$  be the vector beginning in  $x$  and parallel to the vector  $\overrightarrow{cx}$ . Then  $v$  is a continuous function which assigns to every  $x \in S_n$  a vector  $v(x)$  tangent to  $S_n$  in  $x$ . Since  $n$  is even, this is impossible, by the theorem of Poincaré-Brouwer.

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\*) This theorem is used by H. Steinhaus in [4].





# Zum Problem der Impulsübertragung durch unstetige elektromagnetische Wellen in dielektrischen Medien

von

G. MARX und K. NAGY

*Vorgelegt von W. RUBINOWICZ am 6. Dezember 1955*

Kürzlich hat W. Rubinowicz [1] die seit Jahrzehnten diskutierte Frage der Energie- und Impulsverhältnisse der phänomenologischen Elektrodynamik auf Grund bemerkenswerter neuer Gesichtspunkte wieder aufgeworfen. Rubinowicz untersucht die Integralform der Erhaltungssätze im Falle, wo sich in einem Isolator elektromagnetische Sprungflächen bewegen. Der sehr interessanten Rechnung zufolge gibt das elektromagnetische Feld Impuls an die sich bewegende Sprungfläche ab. Der Ausdruck für den in der Zeiteinheit abgegebenen Impuls hat die Form

$$(1) \quad \int_F \left[ P_e \vec{E}' + P_m \vec{H}' + \frac{1}{c} \vec{E} \times \left( \vec{J}_m + \frac{\varepsilon - 1}{4\pi\varepsilon} v \Delta \vec{H} \right) + \frac{1}{c} \left( \vec{J}_e + \frac{\varepsilon - 1}{4\pi} v \Delta \vec{E} \right) \times \vec{H} \right] d\vec{\sigma},$$

wenn man für den Feldimpuls den Abraham'schen Ansatz verwendet. (Siehe die Gl. (3,3) der Rubinowicz'schen Arbeit. Wir benützen die dortigen Bezeichnungen, nehmen aber der Einfachheit halber  $\mu = 1$  an). Man sieht, dass in der Gl. (1) ausser den auf die Flächenladungen  $P_e$ ,  $P_m$  und die Flächenströme  $\vec{J}_e$ ,  $\vec{J}_m$  ausgeübten Kräften noch zwei andere Glieder vorhanden sind, welche mit den Sprüngen der elektrischen und magnetischen Feldstärken  $\Delta \vec{E}$ ,  $\Delta \vec{H}$  ebenfalls in Zusammenhang stehen. Auch im Falle, wo die Flächenströme und Flächenladungen verschwinden und die Sprungfläche sich mit der Lichtgeschwindigkeit  $v = c/\sqrt{\varepsilon}$  fortpflanzt, können die Sprünge der elektrischen und magnetischen Feldstärken an das homogene Medium Impulsbeträge abgeben. Da die Ursache dieser Erscheinung nicht verständlich ist, bedarf das Problem wohl einer ausführlichen Untersuchung.

Bekanntlich können die Elektronen in festen Körpern im Allgemeinen in zwei verschiedenen Zuständen auftreten: entweder als Leitungselektronen, welche sich infolge der Wirkung des Feldes frei bewegen können,

oder als im Molekülinnern gebundene Elektronen. Im letzteren Falle kann das Feld nur im Inneren des Moleküls die Elektronen verschieben und erzeugt so die elektrische Polarisation. Man benützt zur Beschreibung der letzteren Ladungsbewegung den Polarisationsstrom, dessen Raumdichte durch den Ausdruck

$$(2) \quad \frac{\partial \vec{P}}{\partial t} = \frac{\varepsilon - 1}{4\pi} \frac{\partial \vec{E}}{\partial t}$$

gegeben ist. Dieser Strom erzeugt dasselbe magnetische Feld, wie der Leitungsstrom  $\vec{J}_e$ . Im Sinne des Prinzips der Gleichheit von Aktion und Reaktion wirkt das Feld auf diese Ströme zurück. Auf diese Weise entstehen die beiden folgenden Glieder der räumlichen Kraftdichte der phänomenologischen Elektrodynamik [2], [3]:

$$(3) \quad \frac{1}{c} \left[ \vec{J}_e + \frac{\varepsilon - 1}{4\pi} \frac{\partial \vec{E}}{\partial t} \right] \times \vec{H}.$$

Sie sind auch dann gültig, wenn der Strom als Flächenstrom auftritt. Schreitet im Felde ein Sprung der elektrischen Feldstärke  $\Delta \vec{E}$  fort, dann erzeugt er im Dielektrikum einen Zuwachs der Polarisation, d. h. eine Ladungsbewegung. Die entsprechende Polarisationsstromdichte ist:

$$(4) \quad \frac{\varepsilon - 1}{4\pi} v \Delta \vec{E}.$$

In diesem Falle muss auf das Medium an der Sprungstelle der elektrischen Feldstärke eine ebensolche Kraft wirken, wie sie im Falle eines Leitungsstromes auftritt. Das letzte Glied, das in dem von Rubinowicz abgeleiteten Ausdrucke auftritt, entspricht eben dieser Kraftwirkung. Das den Sprung der magnetischen Feldstärke  $\Delta \vec{H}$  enthaltende Glied stammt ebenfalls aus der Wechselwirkung zwischen Feld und Dielektrikum. Dieses Glied entspricht der Kraft, die aus der Theorie der stetig veränderlichen Felder bekannt ist [3], [4] und infolge der Änderung des Polarisationsenergieinhaltes des Dielektrikums entsteht. Diese letztere Wirkung steht mit der Elektrostriktion in engem Zusammenhange. Wenn man annimmt, dass die Polarisierbarkeit (Suszeptibilität) des Mediums der Zahl der in der Volumeneinheit enthaltenen Moleküle, d. h. der Masendichte  $\varrho$  proportional ist

$$(5) \quad \frac{d}{d\varrho} \frac{\varepsilon - 1}{4\pi} = \frac{1}{\varrho} \frac{\varepsilon - 1}{4\pi},$$

dann verschwindet das  $\Delta \vec{H}$  enthaltende Glied, wie man leicht einsehen kann. In diesem Falle (bei verschwindenden Flächenladungen  $P_e, P_m$  und Flächenströmen  $\vec{J}_e, \vec{J}_m$ ) bleibt nur die infolge des Polarisationsstromes

auf das Dielektrikum wirkende Kraft übrig. Da in den Überlegungen von Rubinowicz die Geschwindigkeit des Dielektrikums gleich Null angenommen ist, kann bei der Impulsübertragung keine Arbeitsleistung stattfinden. Die ponderomotorische Kraftwirkung erzeugt in diesem Falle im Dielektrikum elastische Spannungen. Diese durch das Feld im Inneren des Dielektrikums erzeugten Spannungen haben die Verfasser unter Zugrundelegung allgemeiner Bedingungen schon in einer anderen Arbeit [5] bestimmt. Fügt man diese zu dem Energie-Impuls-Tensor des elektromagnetischen Feldes hinzu, dann ist die Impulsänderung des ganzen Systems auch im sprunghaft veränderlichen elektromagnetischen Felde gleich Null. Durch eine einfache Rechnung kann man sich davon mit Hilfe des in [5] enthaltenen Energie-Impuls-Tensors leicht überzeugen.

Zusammenfassend kann man also die folgenden Schlüsse ziehen: Das von Rubinowicz auf Grund des Abraham'schen Energie-Impuls-Tensors abgeleitete Ergebnis steht mit unserer elektronentheoretischen Auffassung über die Struktur der Materie in vollkommener Übereinstimmung. Auf den Polarisationsstrom (2) und (4) (auf bewegte quasielastisch gebundene Elektronen) übt das magnetische Feld die gleiche Kraft aus, wie auf den Leitungsstrom (auf bewegte Leitungselektronen). Dagegen verschwinden im Falle des Minkowski'schen Energie-Impuls-Tensors in der Gl. (1) jene Glieder, welche die Grössen  $\vec{\Delta E}$  und  $\Delta \vec{H}$  enthalten.

Zum Schlusse sei es gestattet, einen Ausspruch von Einstein aus dem Jahre 1908 [2] zu zitieren: „Während ein von einem elektrischen Strom (Leitungsstrom) durchflossener Körper im Magnetfelde eine Kraft erleidet, wäre dies nach Minkowski nicht der Fall, wenn der im Magnetfeld befindliche Körper statt von einem Leitungsstrom, von einem Polarisationsstrom durchsetzt wird. Nach Minkowski besteht also hier ein prinzipieller Unterschied zwischen einem Verschiebungsstrom und einem Leitungsstrom... Dies scheint uns mit dem elektronentheoretischen Bilde nicht in Einklang zu stehen“.

INSTITUT FÜR THEORETISCHE PHYSIK DER ROLAND EÖTVÖS UNIVERSITÄT  
IN BUDAPEST.

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## Thermal Independence of Permittivity of Ferroelectric Heterogeneous Systems

by

Z. PAJAŁ and A. PIEKARA

*Presented by A. SOLTAN on November 19, 1955*

### Introduction

The dielectric properties of ferroelectric solid solutions of barium and strontium metatitanate ( $\text{BaTiO}_3\text{--SrTiO}_3$ ) have recently been subjected to systematic investigation [1], [2], [4]. In spite of the high permittivity of these systems, they can be put to no practical use as condenser materials on account of their large and varying temperature coefficient of permittivity. The aim of this work is to find a method for the preparation of ferroelectric materials with a temperature coefficient of permittivity as small as possible. At the same time, a reasonably high value of the permittivity should be retained. For this purpose, heterogeneous mixtures consisting of different solid solutions of barium and strontium metatitanate were investigated.

### Preparation of samples

Solid solutions of barium and strontium metatitanate with different compositions were prepared from titania, barium and strontium carbonates of c. p. quality. The main impurities were: Si, Mg, Ca, Fe, Sn in titania; Sr, Ca, Mg in barium carbonate and Ba, Ca, Mg, Si, Sn in strontium carbonate \*).

Solid solutions of the desired Curie points were prepared by twofold milling, pressing and sintering the material into the form of tablets at  $1300^\circ\text{C}$ . These were then crushed and passed through suitable sieves. Two such solutions having the same grain size were used for preparing

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\*) As determined in our Laboratory by W. Cierpisz using the spectrographic method.

heterogeneous mixtures. The tablets of heterogeneous material were formed by pressing and sintering in an electric furnace at temperatures

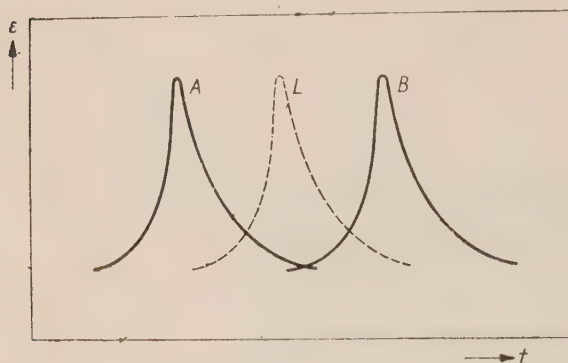


Fig. 1. Schematic diagram of heterogeneous mixture: *A* and *B* represent the curves for the two solid solutions, *L* — the curve for the grain boundary layers

below 1300°C. Strictly speaking, the material obtained consisted of three solid phases: solid solution *A*, solid solution *B*, and the grain boundary layers *L*; the last consisted of a solid solution (*A* + *B*) with a concentration (and Curie point) intermediate between those of *A* and *B* (Fig. 1).

In addition to the solid phases, the material consisted also of a gaseous phase owing to the porosity of the ceramic samples.

#### Results and discussion

The low-frequency bridge method was used for measuring the permittivity of the samples. A frequency of 2 kc. per sec. was supplied to the Schering bridge, the measuring field being 10 V/cm. The samples were placed in an ultrathermostat and the temperature was measured by suitable thermocouples soldered onto the silver electrodes covering the tablets.

The results of the permittivity measurements as a function of temperature are shown in Fig. 2. Curve *A* corresponds to the sample with composition: 33%  $\text{SrTiO}_3$  + 67%  $\text{BaTiO}_3$ ; curve *B* to that of 15%  $\text{SrTiO}_3$  + 85%  $\text{BaTiO}_3$ . The Curie points of these so-

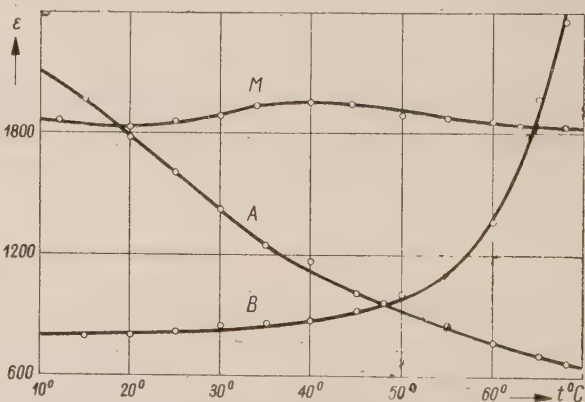


Fig. 2. Permittivity-temperature dependence for the solid solutions *A* and *B* (curves *A* and *B*) and the heterogeneous mixture prepared from 50% *A* + 50% *B* (curve *M*)

lutions were about 0°C. and 70°C. respectively. Curve *M* corresponds to the heterogeneous material consisting of the two different already mentioned solid solutions and the grain boundary layers produced in the process of sintering heterogeneous samples. The sintering temperature of all samples, *A*, *B* and *M*, was 1200°C. It can be seen that the per-



mittivity-temperature dependence for the heterogeneous mixture shows no such sharp maximum as for the simple solid solutions at the Curie temperatures. The flat part of the curve of the heterogeneous system ranges from the lower to the upper Curie temperatures of the two constituents. The average temperature coefficient of permittivity for the system, at temperatures between 15°C. and 65°C., is about 14 times smaller than the respective mean values for the simple solutions. On the other hand, the mean values of permittivity within the same temperature range are 1335 and 1380 respectively for both solid solutions, but attain 1890 for the mixture. All measurements were taken some days after preparation, before ageing of the samples had proceeded. After one and a half year's ageing, the permittivity, as is normally the case in ferroelectrics of this class [3], decreased to about 80% of the initial value; the temperature coefficients, however, retained nearly the same values; the shape of all curves remained the same.

The shape of the permittivity-temperature curve depends on the total volume of the grain boundary layers in the sample. This volume increases as the temperature and time of sintering are increased causing the increase of the permittivity within the temperature range in question. The permittivity of the heterogeneous systems increases simultaneously, owing to a decrease in the porosity of the material. At the

same time, however, there is a marked increase in the temperature coefficient of the samples. To produce samples which will be, to a certain extent, temperature-independent requires a clearly defined sintering regime.

The authors measured the permittivity-temperature dependence for heterogeneous mixtures sintered during various periods of time and at various temperatures. The results of measurements for heterogeneous mixtures consisting of the two solid solutions: 24%  $\text{SrTiO}_3$  + 76%  $\text{BaTiO}_3$  and 30%  $\text{SrTiO}_3$  + 70%  $\text{BaTiO}_3$ , are plotted in Fig. 3. The sintering conditions for the mixtures are as follows:

- |        |     |                  |            |                  |            |
|--------|-----|------------------|------------|------------------|------------|
| sample | I   | — 3 <sup>h</sup> | at 1000°C. | + 2 <sup>h</sup> | at 1100°C. |
| sample | II  | — 6 <sup>h</sup> | at 1000°C. | + 2 <sup>h</sup> | at 1100°C. |
| sample | III | — 3 <sup>h</sup> | at 1000°C. | + 2 <sup>h</sup> | at 1200°C. |

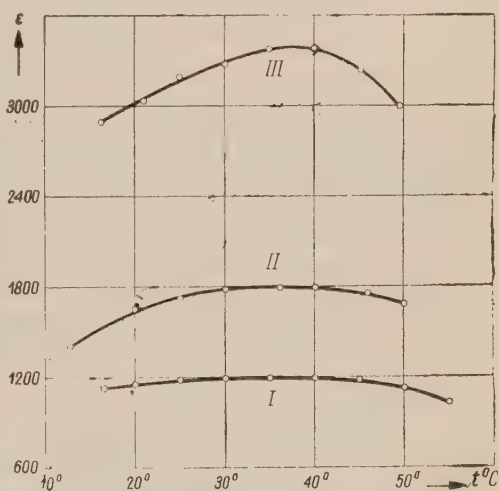


Fig. 3. Permittivity - temperature dependence for heterogeneous mixtures, subjected to various sintering regimes

Later experiments have shown that a further increase in the time and temperature of sintering leads to the trivial case as represented by the formation of the simple solid solution ( $A+B$ ). It can be seen that there exist certain optimum conditions for the sintering of samples, which make it possible to produce heterogeneous ferroelectric systems with a small temperature coefficient and a rather high value of permittivity. Furthermore, it is also possible to produce heterogeneous mixtures with the desired permittivity-temperature response.

Further studies on ferroelectric heterogeneous systems are now in progress and the results will be published shortly.

One of us (Z. P.) wishes to express his thanks to the Polish Academy of Sciences for the award of a research grant.

### Summary

A method is here presented for the preparation of heterogeneous systems consisting of solid solutions of barium and strontium metatitanates. Our aim was to produce ferroelectric materials with a small temperature coefficient of permittivity. Measurements taken by means of the low-frequency bridge method show that these heterogeneous materials have, within a certain range of temperature, a low temperature coefficient of permittivity; the permittivity itself, however, remains at a rather high level.

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## On Hydrogen Bonds in Some Nitroalcohols, (on the Basis of Infra-red Absorption Spectra)

by

T. URBANŃSKI

*Communicated at the meeting of November 28, 1955*

The author formerly expressed the view that there exist intramolecular hydrogen bonds between the nitrogroup and the hydroxyl group (or groups) present in nitroalcohols, which can be formed by adding formaldehyde to nitroparaffins.

This was originally based on the difficulty of forming acetals and katala by some nitrodiols [1] and later on by examination of ultra-violet absorption spectra of a larger number of nitroparaffins and their derivatives [2].

Infra-red absorption spectra of a few nitroparaffins and their derivatives — nitroalcohols in the form of suspension in paraffin-oil — have now been examined by J. Świętosławska, T. Kraczkiewicz and B. Kon-  
tnik (Institute of General Chemistry, Warsaw).

The results obtained are tabulated below. Some typical absorption curves are also reproduced (Figs. 1-6). For purposes of comparison, pentaerythritol (X) (Fig. 7) was examined.

Analysis of the figures leads to the following conclusions:

(1) The very weak band  $n_1$  near to  $7000\text{ cm.}^{-1}$  is present only in those compounds which contain the OH group, or groups.

Repeated measurements confirmed the existence of that band.

According to Ellis and Bath [3], the weak band at  $1.44\text{ }\mu$  (i. e.,  $7000\text{ cm.}^{-1}$ ) in cellulose corresponds to the hydroxyl groups. Nikitin [4] found that bands  $1.48\text{ }\mu$  and  $2.09\text{ }\mu$  (i. e.,  $6757\text{ cm.}^{-1}$  and  $4785\text{ cm.}^{-1}$  respectively) in low nitrated (7.6% N) nitrocellulose could be attributed to hydrogen bonds.

In the light of these observations we think it probable that band  $n_1$  is produced by the hydroxyl groups in compounds II, III, V, VI, VIII, IX and X.

(2) The weak band,  $n_2$ , is probably formed by the addition of bands of lower frequencies, such as  $n_3$ , one of the bands  $n_9-n_{12}$ , and one with



a frequency lower than  $1000\text{ cm.}^{-1}$ . The latter was not investigated in our experiments.

(3) Band  $n_3$  is probably formed by the addition of bands  $n_7$ ,  $n_9$ , e. g. for compound VII,

$$n_3 = 4545, n_7 + n_9 = 4505;$$

for compound IX,

$$n_3 = 4444, n_7 + n_9 = 4449.$$

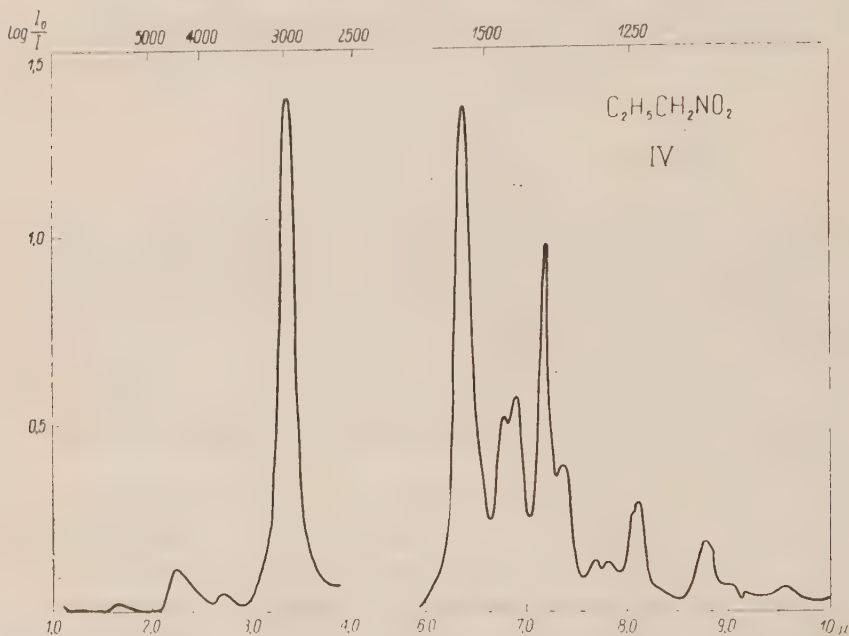
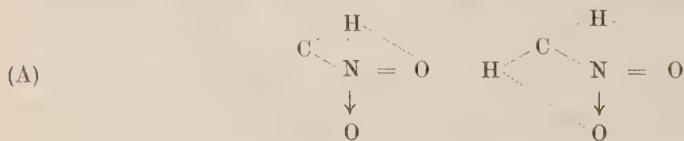


Fig. 1

(4) Band  $n_4$  and  $n_5$  ( $4167$  and  $3704\text{ cm.}^{-1}$  respectively) correspond probably to the bonds between carbon and active hydrogen  $\text{C-H}$  and  $\text{C} \begin{smallmatrix} \text{H} \\ \diagup \end{smallmatrix}$  in secondary and primary nitrocompounds.

It seems that structures (A) with hydrogen bonds between the active hydrogen atom and nitrogroup should be considered. This would be a structure intermediate between the tautomeric forms, normal and *aci*:



The existence of a hydrogen bond would account for the relative weakness of bands  $n_4$  and  $n_5$ .

(5) Band  $n_6$  (3448 or 3333  $\text{cm}^{-1}$ ) is produced by the hydroxyl groups. According to Rodebush [5], the free OH group gives a frequency of 3640  $\text{cm}^{-1}$  and the bonded OH group a frequency of 3330  $\text{cm}^{-1}$ . The latter frequency is near to that of  $n_6$ .

A large number of experiments on the infra-red spectra of glycols were carried out by L. P. Kuhn [6]. The data thus obtained led him to

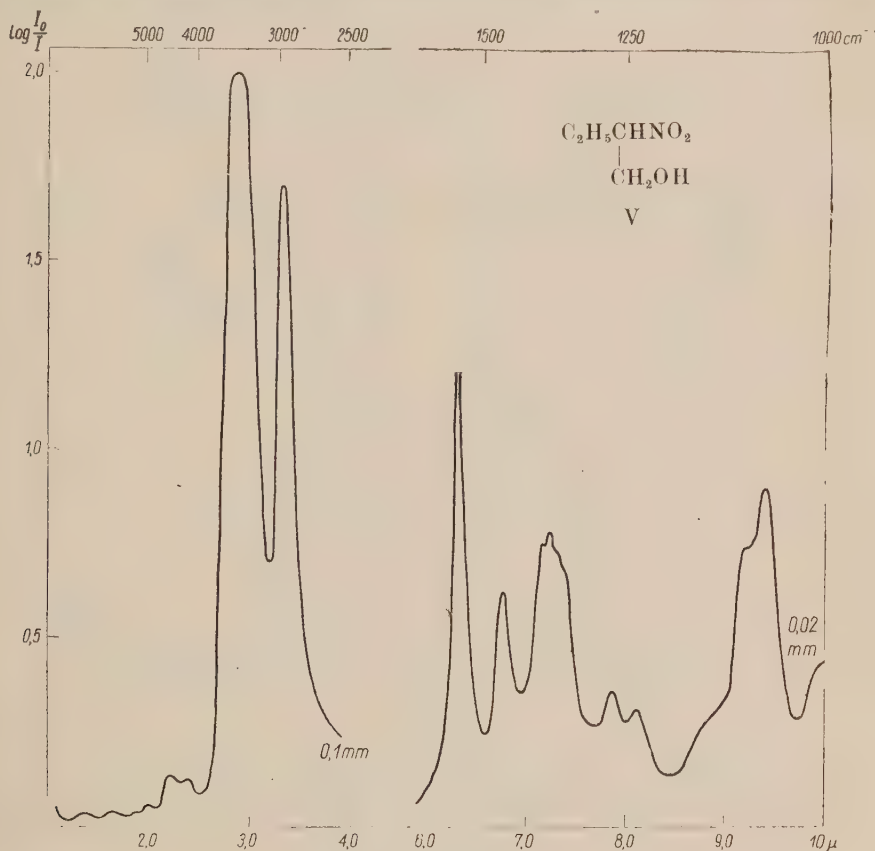
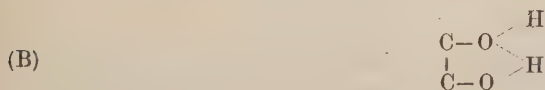


Fig. 2

the conclusion that glycols possess a structure (B), formerly postulated by Davies [7] for pyrocatechol:



The following fact discovered by Kuhn lends support to this view, viz., that the glycols give two absorption bands, if the length of the hydrogen bond (according to the structure B) is less than 3.3 Å. One of these bands is produced by the free OH group (frequency 3600–3644  $\text{cm}^{-1}$ ), the other one — by the bonded OH group (frequency 3448–3612  $\text{cm}^{-1}$ ).

The bonded OH group produces a relatively strong absorption band. In addition, at high concentration or in a solid state, still lower frequencies produced by intermolecular hydrogen bonds may appear.

In our instance two possible structures with intramolecular hydrogen bonds can be postulated: structure (C), which has previously been indicated by the author [2] and structure (D) analogous to Kuhn's structure (B).

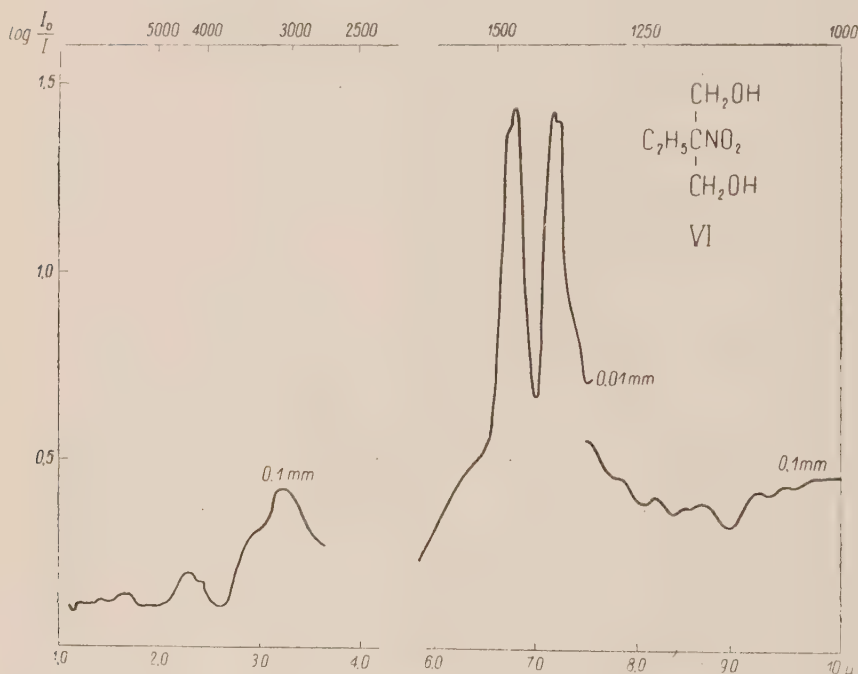
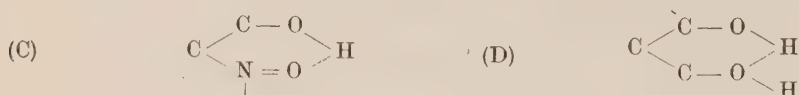


Fig. 3

Also, intermolecular hydrogen bonds should be admitted. They might produce the shifting of the OH bands towards still lower frequencies.

In the monohydric nitroalcohols (II and V) band  $n_6$  is very strong, whereas in the polyhydroxyl alcohols (IX), (X) the band is much weaker and broader, and in the glycols (III) and (VI) it is in the form merely of a bend. A very weak bend  $n_6$  is also observed in compound (VIII) which contains only one OH group.

It is already known in the literature, that bonded hydroxyl groups are often broader than unbonded and the breadth of certain bonded OH bands can be correlated to the strength of the hydrogen bond [6], [8]–[11].



The postulated structures (C) and (D), with two kinds of hydrogen bonds, in compounds (III), (VI), (IX) and (X) are thus in agreement with the already mentioned effect of the decrease in the intensity and broadening of the OH band.

No free hydroxyl groups are present in these compounds and that is probably the reason why no double maxima were noticed for hydroxyl (as found by L. P. Kuhn \*).

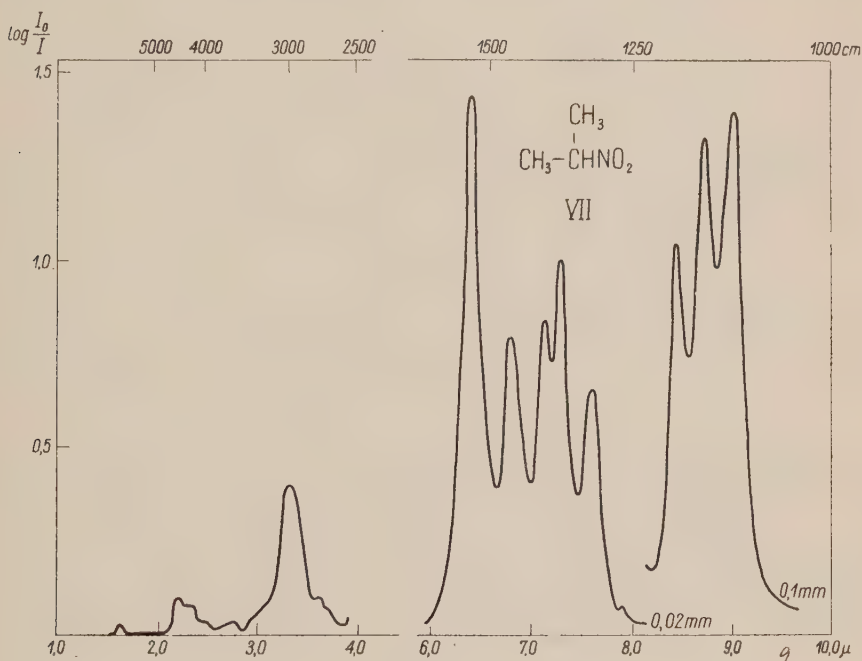
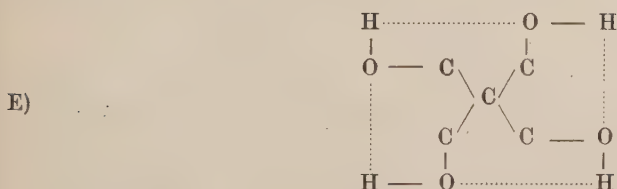


Fig. 4

Structure (E) without any free OH group can be admitted for compound (X).



In monohydroxyl compounds a single hydrogen bond of type (C) without bond (D) should also produce a decrease in the intensity and a broadening of the OH band. This is the case as regards compound (VIII). However, the other two compounds of that type — (II) and (V) —

\*) We have confirmed the result arrived at by Kuhn, viz., that OH groups in ethylene glycol give two maxima.

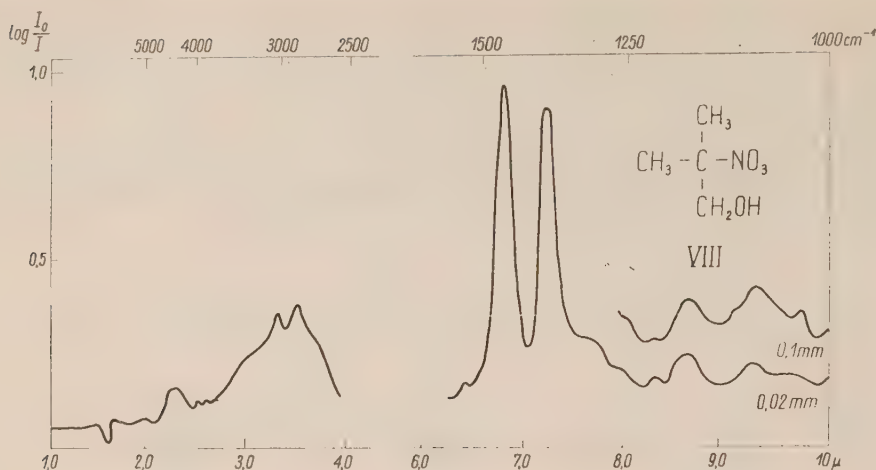


Fig. 5

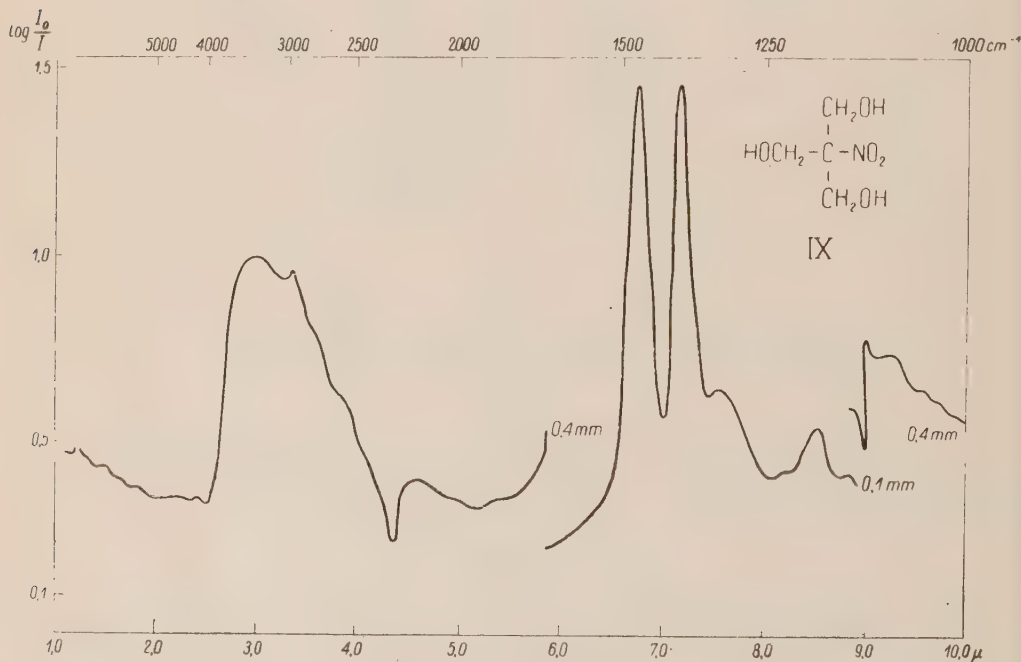


Fig. 6

produce a strong OH band. It is possible to explain this by the presence of the active hydrogen atoms in both compounds. The active hydrogens would form a bond of type (A), which might weaken the bond shown on diagram (C).

The frequency of the NO<sub>2</sub> band ( $\nu_8$ ) of compounds (II) and (V) should not, therefore, differ very much from the frequency of the unbonded NO<sub>2</sub> group, which is actually the case.

(6) The frequency  $n_7$  near  $3000\text{ cm.}^{-1}$  corresponds probably to  $\text{CH}_3$  or  $\text{CH}_2$  stretching vibrations.

(7) Band  $n_8$  is typical for the nitrogroup. In compounds (I), (IV) and (VII), where OH groups are absent, the frequency is  $1567\text{ cm.}^{-1}$ . The same appears in compounds (II), (V) where only one hydroxyl group and active hydrogen atom are present. In compound (VIII), with one hydroxyl group without an active hydrogen atom and in compounds

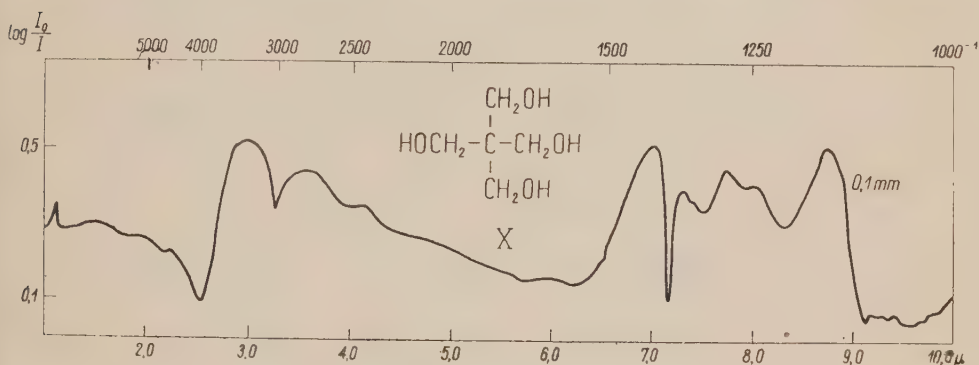


Fig. 7

(III), and (VI), with two hydroxyl groups, the frequency is reduced to  $1555\text{ cm.}^{-1}$  and  $1543\text{ cm.}^{-1}$  respectively. In compound (IX), with three hydroxyl groups, the frequency is also reduced to  $1555\text{ cm.}^{-1}$ .

This is in agreement with the discussion mentioned above under (5) and with the former analysis of the ultraviolet absorption spectra [2].

(8) The bands from  $n_9$  to  $n_{13}$  belong, most likely, to the following vibrations:

$n_9$   $\text{CH}_2$  bending,

$n_{10}$   $\text{CH}_2$  wagging,

$n_{11}$   $\text{CH}_2$  twisting,

$n_{12}$   $\text{CH}_3$  or  $\text{C}-\text{C}$  rocking,

$n_{13}$  the bond  $\text{C}-\text{N}$  between the carbon atom and the nitrogen atom of the nitrogroup.

The author is much indebted to J. Świątosławska, B. Kontnik and T. Krackiewicz for carrying out experiments of infra-red absorption spectra and to W. Sobótka for preparing the pure substances.

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## Frequency of infra-red

No./Figure	Formulae				
		$n_1$	$n_2$	$n_3$	$n_4$
I/—	$\text{CH}_3\text{CH}_2\text{NO}_2$	—	6250	4545	—
II/—	$\begin{array}{c} \text{CH}_3\text{CH NO}_2 \\   \\ \text{CH}_2\text{OH} \end{array}$	7143	6250	4545	4167
III/—	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{CH}_3-\text{C}-\text{NO}_2 \\   \\ \text{CH}_2\text{OH} \end{array}$	6897	6250	4545	—
IV/1	$\text{C}_2\text{H}_5-\text{CH}_2\text{NO}_2$	—	6061	4444	—
V/2	$\begin{array}{c} \text{C}_2\text{H}_5-\text{CH NO}_2 \\   \\ \text{CH}_2\text{OH} \end{array}$	6897	6061	4545	4167
VI/3	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{C}_2\text{H}_5-\text{C}-\text{NO}_2 \\   \\ \text{CH}_2\text{OH} \end{array}$	6897	6061	4444	—
VII/4	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{CH}-\text{NO}_2 \end{array}$	—	6250	4545	—
VIII/5	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{NO}_2 \\   \\ \text{CH}_2\text{OH} \end{array}$	6993	6061	4444	—
IX/6	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{HOCH}_2-\text{C}-\text{NO}_2 \\   \\ \text{CH}_2\text{OH} \end{array}$	6897	6061	4444	—
X 7	$\begin{array}{c} \text{CH}_2\text{OH} \\   \\ \text{HOCH}_2-\text{C}-\text{CH}_2\text{OH} \\   \\ \text{CH}_2\text{OH} \end{array}$	7143	6061	4545	—

absorption bands  $\nu$  cm.<sup>-1</sup>

## B a n d s

$n_5$	$n_6$	$n_7$	$n_8$	$n_9$	$n_{10}$	$n_{11}$	$n_{12}$	$n_{13}$
3704	—	3030	1567	1453	1412	1253	1136	1105
—	3448	3030	1567	1464	1374	1245	1117	1070
—	(3448) *	3030	1543	1464	1383	1245	1130	1081
3704	—	3030	1567	1464	1393	1245	1136	1042
—	3448	2985	1567	1464	1383	1245	1130	1058
—	(3448) *	3125	1543	1464	1383	1208	1143	1075
3704	—	3030	1567	1475	1374	1186	1143	1099
—	(3448) *	2944	1555	1464	1383	1208	1156	1075
—	3333	2985	1555	1464	1393	1215	1156	1099
—	3333	2899	—	1464	1412	1238	1136	—

\*) A bend

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## Classification of Binary Systems with Limited Mutual Solubility

by

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*Communicated by W. ŚWIĘTOSŁAWSKI at the meeting on December 5, 1955*

### Binary systems characterized by limited mutual solubility of the components

Having in view the publication of both experimental and theoretical works dealing with the vapour-liquid equilibrium established in different binary systems, we thought it advisable to extend somewhat the classification of the liquid systems already known [1], since some of the phenomena observed may not be embraced by the existing groups of binary liquid mixtures.

First, it must be emphasized that it happens very often that single systems composed of two components  $A$  and  $H$ , partially miscible in the liquid state, are examined under different pressures and at different temperatures. The shape of the turbidity line is a factor influencing the possible formation of either heteroazeotropes or heterozeotropes, as described by one of us in a monograph [1]. When plotting the concentration  $c_A$  of component  $A$  in the heteroazeotrope against the temperature, we find that with increase of pressure (and of temperature) the curve  $c_A, t$  may, or may not, cross the curve of mutual solubility. If it crosses that line, the heteroazeotrope transforms itself into a homoazeotrope, as shown in Fig. 1a. Some systems may exist where, with an increase of pressure and temperature, the heteroazeotrope transforms itself into a zeotrope. This phenomenon may occur at temperatures lying either below or above the critical solution temperature  $t_E$  (Fig. 1b). Scheme *a* shows the conventional transformation of a heteroazeotrope  $HAz$  into a homoazeotrope lying on the boiling temperature isobar characterized by a two-liquid phase section  $CD$ . Scheme *b* shows a system in which a heteroazeotrope is transformed into a homoazeotrope which, under higher pressure, disappears at a temperature lower than the critical solution one,  $t_E$ . As yet, no experimental evidence has been found for case *b* (Fig. 1) nor have the

physicochemical conditions, which have to be fulfilled, ever been formulated. A graphical presentation of the third case is shown in Fig. 1, scheme *c*. It represents well-known systems, in which no critical solubi-

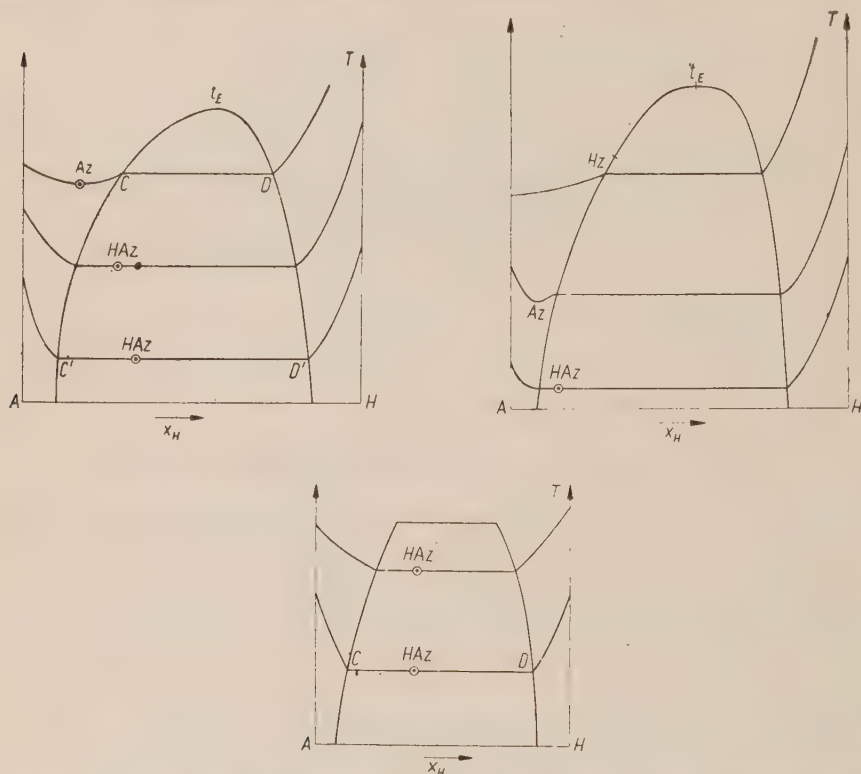


Fig. 1, a, b, c. Various equilibrium diagrams of a single system  $(A, H)$  with pressure changes

lity temperature exists, because one of the liquid phases disappears, reaching its own critical state. In these systems the heteroazeotropy may exist in the whole region in which the two liquid phases coexist with one another.

#### Series of heteroazeotropes $(A, H_i)$

Up to this time no attempt has been made to examine a series of heteroazeotropes  $(A, H_1)$ ,  $(A, H_2)$ , ...,  $(A, H_n)$  composed of an azeotropic agent  $A$  and a series of homologues  $(H)$ . This series is usually represented by the symbol  $(A, H_i)$ . Generally speaking, it is possible to examine the shapes of the boiling temperature isobars, considering them separately for the different mixtures, formed by agent  $A$  with  $H_1, H_2, \dots, H_n$ , respectively. This may be done under atmospheric pressure or under any other deliberately chosen pressure  $p$ .

One can expect a large variety of phenomena associated with the nature both of agent  $A$  and of the series ( $H$ ) of homologues used.

These systems resemble, to some extent, those ( $A, H_i$ ) in which agent  $A$  and homologues  $H_1, H_2, \dots, H_n$  are miscible in all proportions. The main difference consists in the fact that in some ranges of pressure and temperature they are formed by two liquid phases and one gaseous one.

A large amount of theoretical and experimental work has to be done in order to find examples in which there is either an exclusive formation of heteroazeotropes, or else a gradual transition of heteroazeotropes into homoazeotropes and heterozeotropes.

An interesting case will be described by one of us in the near future [2].

It should be added that in ternary systems a greater variety of phenomena is to be expected, on account of the variety of the physicochemical properties of their constituents.

The results obtained from the investigations of the above mentioned systems have some obvious and important practical applications.

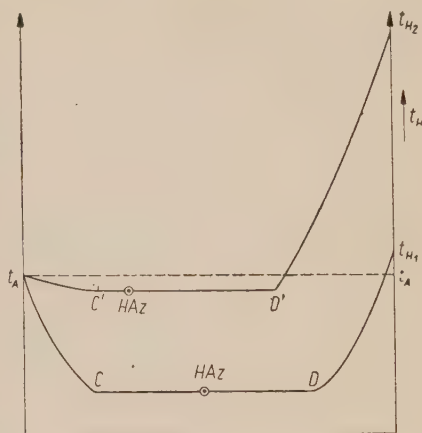


Fig. 2. A series of heteroazeotropes ( $A, H_i$ ) under constant pressure

### Summary

1. A classification is given of binary systems in which there is partial miscibility in the two liquid phases. This classification is based on the behaviour of the liquid vapour-equilibrium of the systems, in which a large range of temperatures and pressures is taken into consideration.

2. The phenomena occurring in the case of a series of binary systems ( $A, H_i$ ) composed of two liquid phases and a vapour one were taken into account.

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## The Anodic Behaviour of Iron in Phosphoric Acid Solutions

by

J. KAMECKI and Z. ZEMBURA

*Presented by B. KAMIENSKI on December 2, 1955*

The behaviour of iron anodes in solutions of acids, bases and salts is one of the problems arising in connection with important technical and theoretical questions in research and in the prevention of iron corrosion. The number of publications devoted to the investigation of iron anodes in various solutions and by the applications of various methods of measurement is considerable.

Among researches over the behaviour of iron anodes in phosphoric acid solutions mention may be made of those of E. Hedges [1] — on the periodic fluctuations in the potential value of iron in 5 per cent  $\text{H}_3\text{PO}_4$  and some experiments on the phosphatization of iron [2].

The present paper continues the investigations previously carried out by us concerning the behaviour of copper [3], zinc [4], and lead [5] anodes in phosphoric acid solutions.

### I. Samples, solutions and methods of measurement

For measurements were used plates of electrolytic iron, about  $25 \times 35 \times 4$  mm. in dimensions, obtained by the galvanic coating of correspondingly smaller steel plates, with iron from a solution of the composition  $\text{FeCl}_2$ —2N,  $\text{CaCl}_2$ —6N, free  $\text{HCl}$ —0.01N, at a current density of 7-8 A/dm<sup>2</sup>, and at a temperature of 90-100°C. The samples were then smoothed with emery papers Nos. 3/0 and 4/0, degreased with trichloroethylene, and polished electrolytically in a sulphuric and phosphoric acid mixture. After polishing, the samples were rinsed first in water and then in alcohol, and rapidly dried in a current of hot air. In order to prevent any diminution of the area of the sample during measurement, the edges were covered with paraffin. The remaining active area of the samples was accurately determined before each measurement.

Two iron cathodes, also of electrolytic iron,  $60 \times 60 \times 4$  mm. in dimensions, were hung vertically one on each side of the anode at a distance from it of about 5 cm.

The measurements were carried out in solutions of 1.00, 3.00, 20.0 and 40.0 N  $\text{H}_3\text{PO}_4$ , and also in 20.00 N  $\text{H}_3\text{PO}_4$ , containing 1 and 2 mols of dissolved Fe per litre of solution.

The apparatus used for the measurements has been described in a previous paper [5].

Measurements of the ratio of the anodic current density and the anodic potential to, first, an increased and then to a diminished electrolysis voltage were carried out 5 minutes after changing the voltage at a temperature of  $20 \pm 1^\circ\text{C}$ . As supplementary tests showed, this period of time makes it possible to measure the values of the current density and anodic potential near stationary values (the most significant changes in these magnitudes occur from 2 to 3 minutes from the time of changing the voltage), and at the same time prevents the passage into solution of any such considerable quantities of iron, as to cause a variation in the results.

The anodic potentials, measured with reference to a saturated calomel electrode, were calculated for the values of the potentials with reference to a normal hydrogen electrode.

## II. Results and discussion

In more dilute solutions of 1.00 and 3.00 N  $\text{H}_3\text{PO}_4$ , the curves of the ratio of the anodic current density to the voltage (for example those given in Fig. 1) are in shape different from the curves obtained in more concentrated solutions of 20.0 and 40.0 N  $\text{H}_3\text{PO}_4$  saturated with iron to a varying degree (for example the curves given in Fig. 2).

In 1.00 and 3.00 N  $\text{H}_3\text{PO}_4$ , the current density at first rises linearly (with an insignificant deviation caused by concentration polarization), together with the increase in the voltage (Fig. 1). At a voltage of about 5.5 V for 1.00 N  $\text{H}_3\text{PO}_4$ , and about 3.9 V for 3.00 N  $\text{H}_3\text{PO}_4$  acid, there occurs a sudden decrease in density to about half the initial value. Oxygen begins to be given off vigorously. The subsequent increase in the density is again linear.

If a decrease in the voltage is applied, the course of the density curve is somewhat different (heavy dots in Fig. 1). Up to about 2.4 V, there is observed an almost linear drop in the density, which then becomes stabilized at very low values (0.24–0.05 mA/cm.<sup>2</sup>). At about 0.9 V for 1.00 N  $\text{H}_3\text{PO}_4$ , and 0.7 V for 3.00 N  $\text{H}_3\text{PO}_4$ , the density suddenly increases to values corresponding to those measured in the first part of the measurements for the rising voltages. The characteristic loop of the electrochemical "hysteresis" of density is obtained.

In solutions of 20.0 (Fig. 2) and 40.0 N  $\text{H}_3\text{PO}_4$ , as well as in 20.0 N  $\text{H}_3\text{PO}_4$  containing 1 and 2 mols Fe per litre of solution, the course of the anodic density curves varies so much that a distinct plateau section of density is marked on them (density approximate to the independent constant of the voltage). The voltage at which the inflection in the density curve decreases (about 1.0 V for 20.0 N  $\text{H}_3\text{PO}_4$  and 0.7 V for 40.0 N  $\text{H}_3\text{PO}_4$ ) and the plateau section reaches 2.0 to 2.5 V. Then begins a linear increase in the density, associated with vigorous evolution of oxygen. For falling voltages, the density values coincide with those obtained for rising voltages, but "hysteresis" density loops do not appear in these solutions.

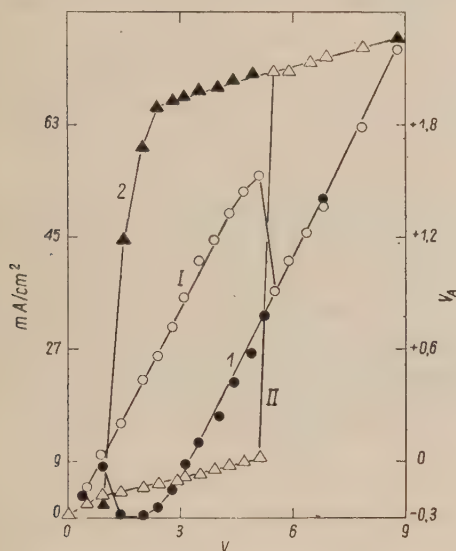


Fig. 1. Anodic current density (I, 1) and anodic potential (II, 2) vs. voltage in solutions of 1.00 N  $\text{H}_3\text{PO}_4$ . I and II = curves for rising voltage. 1 and 2 = curves for falling voltage

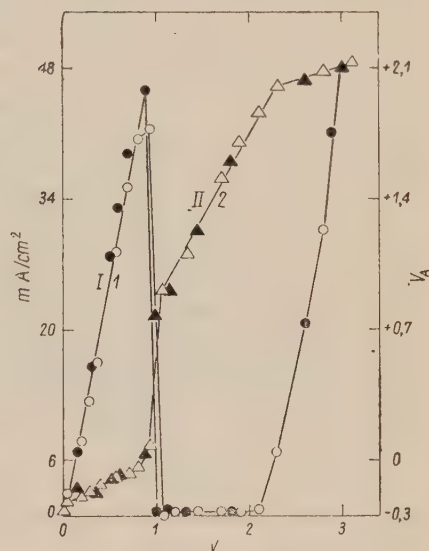


Fig. 2. Anodic current density (I, 1) and anodic potential (II, 2) vs. voltage in a solution of 20.0 N  $\text{H}_3\text{PO}_4$ . I and II = curves for rising voltage. 1 and 2 = curves for falling voltage

The anodic potential curves are, in all the solutions mentioned, inflected according to the changes observed in the course of the anodic current density curves. For increased voltages, the anodic potential rises at first slowly from the mean value of  $-0.27$  V observed before electrolysis begins, to values of about  $+0.01$ ,  $-0.05$ ,  $-0.02$ ,  $-0.05$ ,  $-0.09$ ,  $-0.10$  V for solutions of 1.00, 3.00, 20.0 and 40.0 N  $\text{H}_3\text{PO}_4$ , as well as for 20.0 N  $\text{H}_3\text{PO}_4$  with the addition of 1 and 2 mols Fe per litre of solution. Subsequently it rises quickly to the following values:  $+2.08$ ,  $+2.07$ ,  $+2.00$ ,  $+1.99$ ,  $+2.06$ ,  $+2.09$  V for the solutions previously mentioned. While oxygen is being given off, there is an insignificant rise in the potential. The region of the linear increase in the potential, already described, corresponds to the inflection of the density curve in the two more dilute solutions, and

to the plateau section in the concentrated solutions, except that in these last it again divides into two straight sections. The point of intersection of the straight sections corresponds to a potential of about  $+0.7$  V for solutions of 20.0, 40.0 N  $\text{H}_3\text{PO}_4$ , and of 20.0 N  $\text{H}_3\text{PO}_4$  with additions of iron, and lies at the beginning of the density plateau.

As in the case of the density, the "hysteresis" loops of the potential appear only for the two more dilute solutions. In the concentrated solutions, the curves of the potential for both increasing and decreasing voltages coincide.

As has already been observed in previous papers [4], [6], an increase in the quantity of anodic metal dissolved in the electrolyte causes a drop in the density curves, without changing either their shape or the succession of anodic processes. The values of the anodic potential do not depend in practice on the amount of iron dissolved in the electrolyte, and thus the curves of the potential coincide in the three solutions investigated.

In all the solutions investigated, experiments concerning electrolytic polishing were carried out. It was found that polishing specimens of iron in solutions of 20.0 and 40.0 N  $\text{H}_3\text{PO}_4$  was possible in conditions of current corresponding to the rising portion of the density-voltage curve, at the time of evolution of oxygen. In plateau conditions, a lustre appears also on the samples; the process of polishing is, however, slow on account of the insignificant density of current corresponding to this section of the curve.

It seems probable, on the basis of the observations given above, that on iron anodes the following processes take place in proportion to the rise in the voltage:

1. Until the first inflection on the density curve has been attained, the anode is in an active state and passes into solution chiefly in the form of  $\text{Fe}^{++}$  ions. This is also indicated by direct determination of the  $\text{Fe}^{++}$  ions in the solution;

2. As a result of concentration polarization, the anodic potential rises sufficiently to make possible reactions leading to oxidation. Reactions of the following type are therefore possible here:



On the basis of the material quoted, it is not possible to decide which of the reactions mentioned are proper for the processes investigated. It seems, however, that the passive layer is not oxygen but an oxide, since to accept the latter makes it possible to elucidate the ap-



pearance of the "hysteresis" loops of the potential and density in dilute solutions of  $\text{H}_3\text{PO}_4$ ;

3. The inflection at about  $+0.7$  V, described above, on the curves of the potential in more concentrated solutions, may perhaps correspond to the reaction of oxidation of  $\text{Fe}^{++}$  from the solution into  $\text{Fe}^{+++}$  on an already inert electrode;

4. The construction of the passive layer is completed before the evolution of oxygen begins.

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## Relation Between the Electric Conductivity and Catalytic Activity of $\text{ZnO}—\text{Cr}_2\text{O}_3$ Mixed Catalysts

by

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In the previous publications [1], [2] of two of the present authors, with A. Bielański, it was proved that a distinct parallelism exists between, on the one hand, the changes in electric conductivity of  $\text{ZnO} + \text{Fe}_2\text{O}_3$  and  $\text{MgO} + \text{Cr}_2\text{O}_3$  mixtures working as catalysts in the reaction of dehydrogenation of  $\text{C}_2\text{H}_5\text{OH}$ , and on the other—the yield of the catalytic reaction. The catalyst used in the first investigation was a mixture of two oxides showing electronic (normal) conduction. The introduction of the vapours of the reactants into the reaction chamber was followed by an increase in the electric conductivity of the catalyst. In the course of the second investigation, a mixture of two oxides, both abnormal semiconductors, was applied as catalyst. In the temperature range up to  $500^\circ\text{C}$ . a decrease in conductivity was observed after the reacting vapours were introduced into the reaction chamber. In higher temperatures, the conductivity of a catalyst rich in  $\text{Cr}_2\text{O}_3$  decreased to begin with and then increased up to a level above that initially recorded. In the case of both normal semiconductors and abnormal semiconductors a distinct correlation was found between the changes in electric conductivity of the working catalyst and the yield of catalytic reaction. The indications of the changes in conductivity observed in those investigations were in agreement with those anticipated in the theoretical treatment given by Hauŕfe [3], but it is difficult to interpret them on the basis of the Volkenstein [4] concepts.

The catalyst used in the present investigation was a mixture of two oxides, one normal semiconductor ( $\text{ZnO}$ ) and one — abnormal semiconductor ( $\text{Cr}_2\text{O}_3$ ). The reagents used were pharmacopoeial zinc oxide, the same preparation as in [1] and chromic oxide (Merck, *pro analisi*), the same preparation as used in [2]. The apparatus and technique of measurement were as described in another paper [1]. Investigations were made on catalysts of the following compositions:  $4\text{ZnO} + \text{Cr}_2\text{O}_3$ ,

$3\text{ZnO} + \text{Cr}_2\text{O}_3$ ,  $2\text{ZnO} + \text{Cr}_2\text{O}_3$ ,  $\text{ZnO} + \text{Cr}_2\text{O}_3$ ,  $\text{ZnO} + 2\text{Cr}_2\text{O}_3$ ,  $\text{ZnO} + 3\text{Cr}_2\text{O}_3$ ,  $\text{ZnO} + 4\text{Cr}_2\text{O}_3$ , as well as on pure  $\text{ZnO}$ . The measurements of the conductivity of the catalyst and of the catalytic reaction yield were carried out within a temperature range of from  $250^\circ$  to  $550^\circ\text{C}$ . In all the measurements, the same reactant was used, i.e., 20% ethyl alcohol-water mixture. The reaction products consisted mainly of acetaldehyde. After passing 20 ml. of 20% alcohol-water mixture through the apparatus, the content of  $\text{CH}_3\text{CHO}$  in the condensation products was determined, by means of hydroxylamine hydrochloride and the results expressed in mg.  $\text{CH}_3\text{CHO}$ . This value was subsequently taken as the measure of the reaction yield.

Fig. 1 shows as a function of time, the change in the logarithm of the conductivity of the catalysts which took place after the reacting

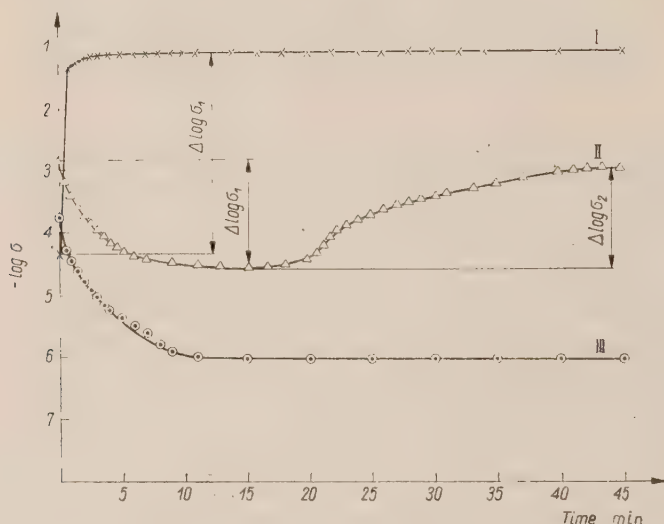


Fig. 1. Change in  $\log \sigma$  of the catalyst in the course of the reaction of dehydrogenation of ethyl alcohol vapours

vapours were introduced into the reaction chamber. Curve I was taken for pure  $\text{ZnO}$  at a temperature of  $400^\circ\text{C}$ . Similar curves were also obtained at all other temperatures, with catalysts consisting of pure  $\text{ZnO}$ , and for catalysts of compositions  $4\text{ZnO} + \text{Cr}_2\text{O}_3$ ,  $3\text{ZnO} + \text{Cr}_2\text{O}_3$ , and  $2\text{ZnO} + \text{Cr}_2\text{O}_3$ . The shape of the  $\log \sigma$ -time relation for catalysts of compositions  $\text{ZnO} + 2\text{Cr}_2\text{O}_3$ ,  $\text{ZnO} + 3\text{Cr}_2\text{O}_3$ , and  $\text{ZnO} + 4\text{Cr}_2\text{O}_3$ , as well as for pure  $\text{Cr}_2\text{O}_3$  are shown by curve III at temperatures below  $450$ – $500^\circ$ , and by curve II at higher temperatures. Curves II and III represent the behaviour of the  $\text{ZnO} + 4\text{Cr}_2\text{O}_3$  mixture at  $450^\circ$  and  $350^\circ$  respectively.

In the case of catalysts of the compositions  $\text{ZnO} + \text{Cr}_2\text{O}_3$ , at a temperature of  $250^\circ$ , the  $\log \sigma$ -time curve was obtained – analogous to curve II; within the temperature range  $300$ – $500^\circ$  – analogous to curve III; and at a temperature of  $550^\circ$  – again analogous to curve II.



In the case of samples rich in ZnO, the increase in the conductivity of the catalyst was observed after the reacting vapours were introduced into the reaction chamber. A similar change in conductivity was observed with catalysts which were electronic semiconductors [1]. In the case of samples rich in  $\text{Cr}_2\text{O}_3$ , the conductivity decreased at lower reaction temperatures and in the higher temperatures first decreased and then increased. This behaviour is similar to that which we observed with catalysts with positive hole conduction [2].

Fig. 2 shows, for the mixture  $3\text{ZnO} + \text{Cr}_2\text{O}_3$ , the dependence of the absolute value of  $\Delta \log \sigma$ , (normal line) and of the reaction yield (dotted line) on the reaction temperature.

There was similarity between the shape of  $|\Delta \log \sigma_1|$ -temperature and reaction yield-temperature curves obtained for, on the one hand, pure ZnO and, on the other, for  $4\text{ZnO} + \text{Cr}_2\text{O}_3$  mixture.

As Fig. 2 shows, the greater the  $|\Delta \log \sigma_1|$  value, the greater is the reaction yield. The maximum on the conductivity curve corresponds to the maximum on the reaction yield curve. In the temperature range observed, a linear relationship may be assumed between the  $|\Delta \log \sigma_1|$  values and the reaction yield within the temperature range observed.

In the case of  $\text{Cr}_2\text{O}_3$ -rich catalysts, the character of curves representing, on the one hand, the absolute value of  $\Delta \log \sigma_1$ , and, on the other, the reaction yield as a function of the reaction temperature, visibly changes. Fig. 3 shows these functions for the mixture of the composition  $\text{ZnO} + 4\text{Cr}_2\text{O}_3$ . The dotted line (curve I) shows the dependence of the catalytic reaction yield on the reaction temperature. The yield increases up to a maximum at about  $450^\circ$ , and then decreases. The normal lines (curves II and III) show the change in  $|\Delta \log \sigma_1|$  and  $|\Delta \log \sigma_1| + |\Delta \log \sigma_2|$  values respectively. The graph of  $|\Delta \log \sigma_1| + |\Delta \log \sigma_2|$  values is plotted for temperatures above  $400^\circ$ . Within this range of temperatures,  $|\Delta \log \sigma_2|$  has an almost constant value.

The curves in Fig. 3 indicate that, in the region of lower temperatures ( $250$ - $400^\circ$ ), the decrease in the conductivity is accompanied by an increase in catalytic reaction yield. The dependence of the two values may be taken as linear. At temperatures above  $400^\circ$ , the decrease in

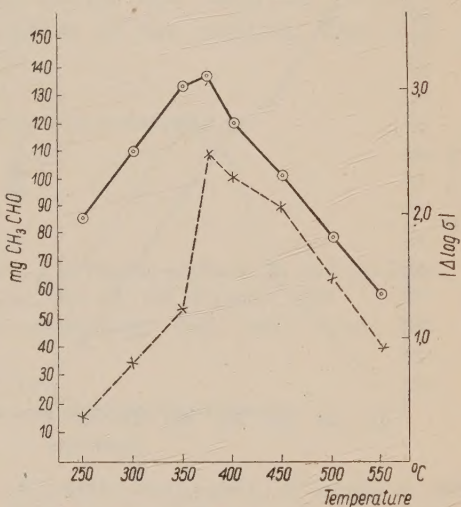


Fig. 2. Changes of the  $|\Delta \log \sigma_1|$  value for  $3\text{ZnO} + \text{Cr}_2\text{O}_3$  mixture (normal line) and catalytic reaction yield (dotted line), both as a function of the reaction temperature

$|\Delta \log \sigma_1|$  and  $|\Delta \log \sigma_1| + |\Delta \log \sigma_2|$  values corresponds to the decrease in the reaction yield. Also, in this temperature range, the dependence of the two values is linear, the directional coefficient being different in

each case. Similar curves were obtained with the mixtures  $\text{ZnO} + \text{Cr}_2\text{O}_3$ ,  $\text{ZnO} + 3\text{Cr}_2\text{O}_3$  and with pure  $\text{Cr}_2\text{O}_3$ .

These results refer to catalysts rich in ZnO, i. e. rich in normal semiconductor, and on the other hand to the  $\text{Cr}_2\text{O}_3$ -rich catalysts, i. e. rich in abnormal semiconductors.

The behaviour of catalysts of intermediate compositions, i. e.  $\text{ZnO} + \text{Cr}_2\text{O}_3$  and  $2\text{ZnO} + \text{Cr}_2\text{O}_3$ , was different. In Fig. 4 are shown the curves for the mixture  $2\text{ZnO} + \text{Cr}_2\text{O}_3$ , and in Fig. 5 for the mixture  $\text{ZnO} + \text{Cr}_2\text{O}_3$ .

With samples of the composition  $2\text{ZnO} + \text{Cr}_2\text{O}_3$ , the catalytic reaction yield increased up to a maximum at about  $450^\circ$  and then decreased. The  $|\Delta \log \sigma_1|$  values decreased with the increasing temperature. With the samples of the composition  $\text{ZnO} + \text{Cr}_2\text{O}_3$ , the reaction yield increased

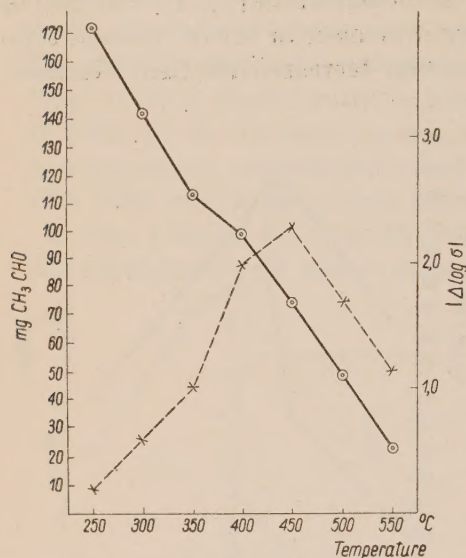


Fig. 3. Change in  $|\Delta \log \sigma_1|$  and  $|\Delta \log \sigma_1| + |\Delta \log \sigma_2|$  values for  $\text{ZnO} + \text{Cr}_2\text{O}_3$  mixture (normal line) and the catalytic reaction yield (dotted line), both shown as functions of the reaction temperature

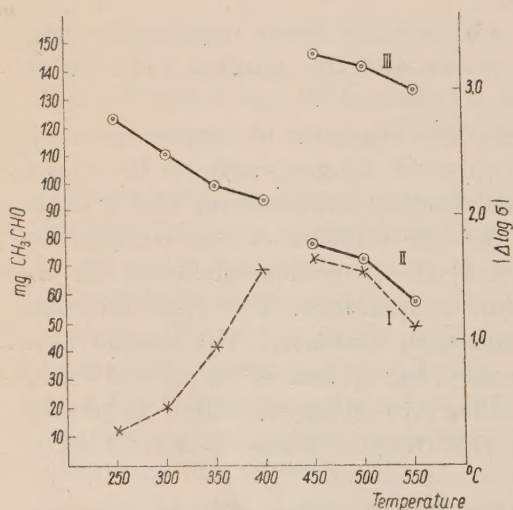


Fig. 4. Dependence of catalytic reaction yield (dotted line) and  $|\Delta \log \sigma_1|$  values (normal line) for the mixture  $2\text{ZnO} + \text{Cr}_2\text{O}_3$  on the temperature of the reaction

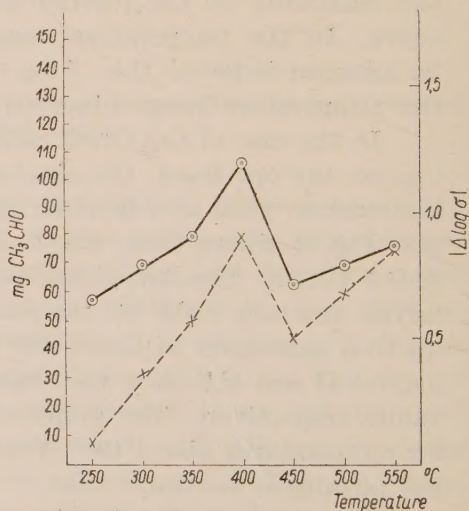


Fig. 5. Dependence of catalytic reaction yield (dotted line) and  $|\Delta \log \sigma_1|$  values (normal line) for the mixture  $\text{ZnO} + \text{Cr}_2\text{O}_3$  on the temperature of the reaction



up to a local maximum at about  $400^\circ$ , then decreased to a minimum at  $450^\circ$  and increased again. The curve representing the changes in the  $|\Delta \log \sigma_1|$  values is similar in shape.

In both cases, the linear relationship may be assumed to be between the  $|\Delta \log \sigma_1|$  values and the catalytic reaction yield.

During the investigations, there was also observed a marked parallelism between the changes in  $|\Delta \log \sigma|$  values and catalytic reaction yield, both as a function of the composition of the catalyst. This will be the subject of our next paper.

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